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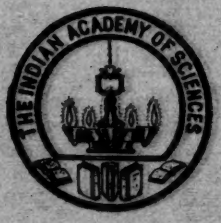

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THE ATOMIC HEATS OF GOLD, PLATINUM AND ANTIMONY AT LIQUID HELIUM TEMPERATURES

By K. G. Ramanathan, F.A.Sc. and T. M. Srinivasan

(National Physical Laboratory, New Delhi)

Received November 19, 1958

Introduction

The specific heat of platinum was measured in the liquid helium range of temperature by Kok and Keesom as early as 1936 while that of gold was measured only very recently by Corak *et al.* (1955). Apart from these two measurements no other calorimetric data appear to be available for these two metals in the liquid helium range. Therefore, it was decided to obtain fresh measurements with a view to provide an independent check on the earlier data using the new vacuum calorimeter (Ramanathan and Srinivasan, 1955) developed in this laboratory.

Travis Anderson (1930) investigated the temperature variation of the specific heat of antimony in the range 60° to 300° K. Below this range, however, no data appear to be available. So, the investigation of the temperature variation of atomic heat of antimony in the liquid helium range was also carried out with the purest available metal, using our calorimeter.

Experimental Details

The new vacuum calorimeter which is capable of an accuracy of over 3 per cent. in the temperature range 1·2 to 4·2° K. has been fully described in an earlier communication (Ramanathan and Srinivasan, 1955).

The specimens of gold and platinum were supplied by Messrs. Johnson Matthey & Co., Ltd., London, in cylindrical forms with diametrical holes for embedding carbon resistance thermometers. The purity of the gold specimen is 99·97 per cent. and it weighs 67·99 gm. The platinum specimen is 99·99 per cent. pure and weighs 74·88 gm. The antimony specimen of mass 33·92 gm. was cast out of a Johnson Matthey sample of 99·6 per cent. purity.

The resistance thermometer (a ½ watt, 100 ohms resistor manufactured by Speer Resistor Corporation, U.S.A.) was calibrated against the 1948 vapour pressure-temperature scale (Van Dijk and Shoenberg, 1949) and corrected to the 1955 scale (Van Dijk and Durieux, 1955).

RESULTS

Gold and Platinum.—Figures 1 (*a*) and (*b*) show the variation of the atomic heats of gold and platinum respectively in the liquid helium range of temperature.

The atomic heats of these elements can be represented by the equation $C_v = aT + bT^3$, where '*a*' and '*b*' are the constants corresponding to

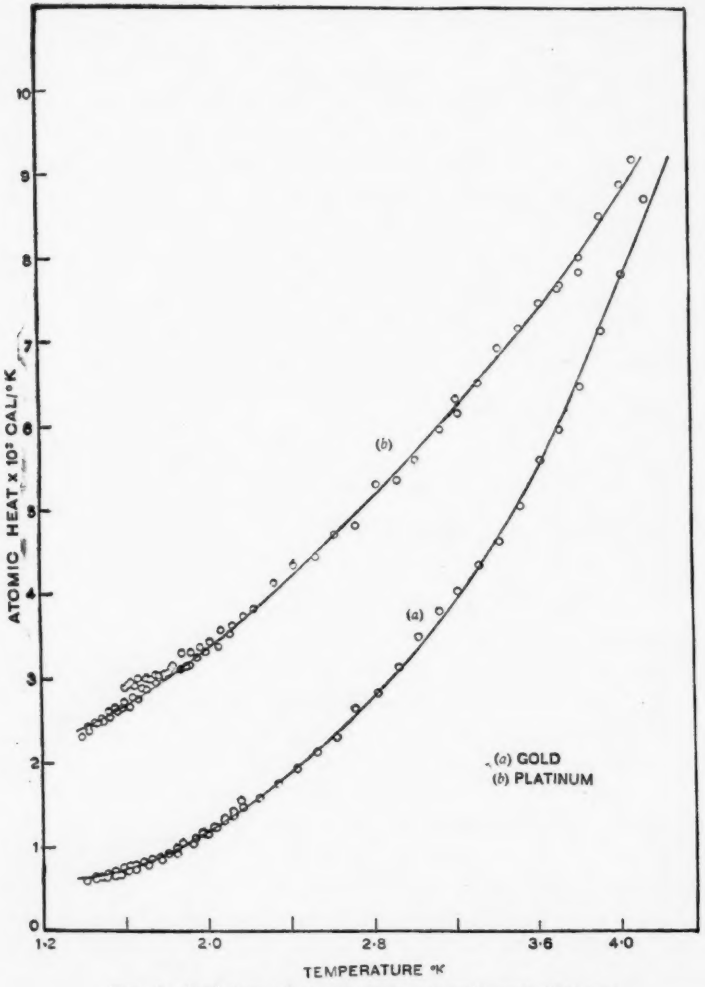

FIG. 1. Variation of atomic heats of gold and platinum.

the electronic and lattice contributions and 'T' is the absolute temperature.

It is noticed from the graphs that the specific heat of the monovalent noble metal gold falls off more rapidly than the specific heat of the transition metal, platinum. This indicates a much larger linear term in the specific heat equation for platinum and is consistent with the supposition of Mott and Jones (1936) that the unfilled '*d*' band contributes appreciably to the electronic specific heats of transition metals.

The atomic heat constants of gold have been calculated by the method of least squares from the results in the range 1·3 to 4·2° K. and are found to be

$$a = (1{\cdot}825 \pm 0{\cdot}069)\ 10^{-4}$$
$$b = (1{\cdot}049 \pm 0{\cdot}010)\ 10^{-4}$$

The Debye temperature calculated from the '*b*' value ($b = 464{\cdot}4/\theta^3$) is 164·2° K.

Similarly the constants of platinum are found to be

$$a = (15{\cdot}956 \pm 0{\cdot}100)\ 10^{-4}$$
$$b = (\ 0{\cdot}337 \pm 0{\cdot}014)\ 10^{-4}$$

and

$$\theta = 239{\cdot}7°\ \text{K.}$$

The results of earlier workers together with ours are given in Table I for comparison.

TABLE I

	Gold			Platinum		
	Purity %	$a \times 10^4$	$\theta°$ K.	Purity %	$a \times 10^4$	$\theta°$ K.
This work ..	99·97	1·825	164·2	99·99	15·956	239·7
Corak *et al.* ..	99·99	1·777	164·57	..	..	..
Schultz (1954)		1·48	..	..	..	..
Kok and Keesom (1936)		..	..	99·95	16·07	233·0
Burton (1940)		..	(S.H.) 170 (Res.) 175	..	..	(S.H.) 225 (Res.) 240

S.H.—Value derived from specific heat data.

Res.—Value derived from electrical resistivity by Gruneisen's formula.

The electronic specific heat constants and the Debye θ values of gold and platinum of earlier workers show general agreement with our values.

Antimony.—Figure 2 (*a*) shows the variation of the atomic heat of antimony with temperature in the range 1·3 to 4·2° K. Figure 2 (*b*) is a plot

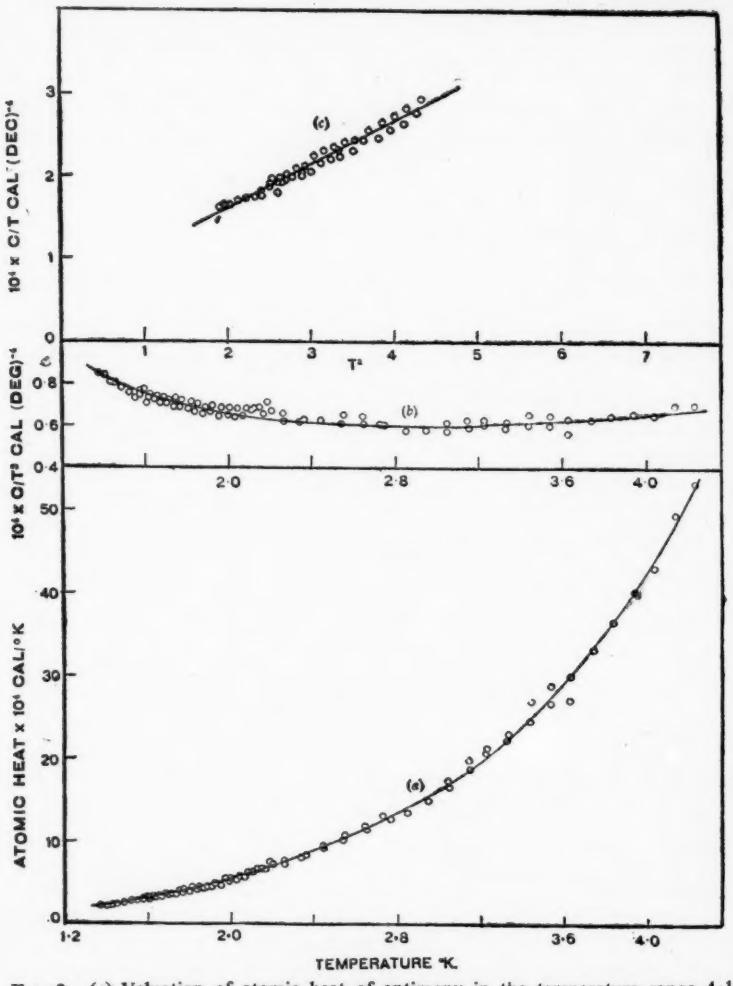

FIG. 2. (*a*) Valuation of atomic heat of antimony in the temperature range 4·1–1·3° K.
(*b*) Variation of C/T^3 with temperature.
(*c*) Plot of C/T against T^2.

of C_v/T^3 against T. The region where the electronic contribution becomes predominant appears below 2° K. Figure 2 (*c*) is a plot of C_v/T *versus* T^2 in this region.

The constants have been calculated by the method of least squares from all the measurements below 2° K. and are found to be

$$a = (0{\cdot}575 \pm 0{\cdot}041)\ 10^{-4}$$

$$b = (0{\cdot}525 \pm 0{\cdot}013)\ 10^{-4}$$

and

$$\theta = 206{\cdot}8^\circ \text{ K.}$$

Burton (1940) has calculated θ as 201° K. from the specific heat data of Travis Anderson (1930). This is also in good agreement with our result.

Summary

The variation of atomic heats of gold, platinum and antimony have been investigated in the liquid helium range of temperature (4·2 to 1·3° K.). The atomic heats of these elements can be represented by the formula

$$C_v \text{ (Gold)} = 10^{-4}\,[(1{\cdot}825 \pm 0{\cdot}069)\,T + (1{\cdot}049 \pm 0{\cdot}010)\,T^3] \text{ Cal./° K.}$$

$$C_v \text{ (Platinum)} = 10^{-4}\,[(15{\cdot}956 \pm 0{\cdot}100)\,T + (0{\cdot}337 \pm 0{\cdot}014)\,T^3] \text{ Cal./° K.}$$

$$C_v \text{ (Antimony)} = 10^{-4}\,[(0{\cdot}575 \pm 0{\cdot}041)\,T + (0{\cdot}525 \pm 0{\cdot}013)\,T^3] \text{ Cal./° K.}$$

Acknowledgment

The authors are thankful to Sir K. S. Krishnan, F.R.S., Director, National Physical Laboratory, for his kind interest in this work.

References

Burton, E. F., Grayson Smith, H. and Wilhelm, J. O. — *Phenomena at the Temperature of Liquid Helium* (Reinhold Publishing Corporation, New York), 1940, p. 348.

Corak, W. S. *et al.* .. — *Phy. Rev.*, 1955, **98**, 1699.

Kok, J. A. and Keesom, W. H. — *Physica*, 1936, **3**, 1035; Leiden Comm. No. 245 (*a*).

Mott, N. F. and Jones, H. .. — *The Theory of the Properties of Metals and Alloys* (Oxford University Press), 1936, p. 192.

Ramanathan, K. G. and Srinivasan, T. M. — *Phil. Mag.*, 1955, **46,** 338.

Schulz, L. G. .. *Phy. Rev.*, 1954, **94,** 1422.

Travis Anderson, C. .. *J. Am. Chem. Soc.*, 1930, **52,** 2712.

Van Dijk, H. and Durieux, M. — *Comm. Conference de Physique des Basses Temperatures, Paris,* 1955, p. 595.

—— and Shoenberg, D. .. *Nature*, 1949, **164,** 151.

LATTICE AND ELECTRONIC SPECIFIC HEATS OF ZINC AND CADMIUM

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Received November 19, 1958

(Communicated by Dr. K. G. Ramanathan, F.A.SC.)

Introduction

The temperature variation of the specific heats of the metallic elements can be represented by the equation $C_v = aT + bT^3$, where 'a' and 'b' are the constants of the electronic and lattice specific heats respectively and 'T' is the absolute temperature. The values of these constants are usually determined from the experimental specific heats of the metal measured at various temperatures.

Keesom and Van den Ende (1932) were the earliest to measure the atomic heat of zinc at liquid helium temperatures. Silvidi and Daunt (1950) investigated the atomic heat variation of zinc powder in the range 1·2 to 4° K. to determine the lattice and electronic specific heat constants. Daunt and Heer (1949) have thermodynamically computed the electronic specific heat constant from their investigation of the threshold field curve. In comparing the results of these measurements it became necessary to conduct a fresh investigation of the temperature variation of the atomic heat of zinc in the range 1·2 to 4·2° K. using a new technique described in detail in an earlier publication (Ramanathan and Srinivasan, 1955).

Lange and Simon (1928) and Craig *et al.* (1954) measured the specific heat of cadmium down to liquid hydrogen temperatures. But, in the helium range the only available data appear to be that of Smith and Wolcott (1956) who investigated this metal between 1° and 12° K. From the investigation of the threshold curve, Goodman and Mendoza (1951), Samoilov (1952) and Smith and Daunt (1952) have computed the specific heat contribution due to the conduction electrons in the normal state. For comparing the calorimetric and magnetic values, a fresh measurement of the specific heat of cadmium has been carried out in the liquid helium range.

Experimental Details

The accuracy of the measurements, made with the new vacuum calorimeter referred above, is estimated to be better than 3% in the temperature

range 1·2 to 4·2° K. The carbon resistance thermometer (100 ohm, ½ watt, Speer Resistor Corporation, U.S.A.) is calibrated against the 1948 vapour pressure-temperature scale (Van Dijk and Shoenberg, 1949).

The specimens of zinc and cadmium were cast out of samples (obtained from Messrs. Johnson Matthey & Co., Ltd., London) of purity 99·95% with a diametrical hole for the carbon thermometer. The masses of the zinc and cadmium specimens were 42·57 gm. and 50·44 gm. respectively.

RESULTS

Figure 1 (*a*) shows the temperature variation of the specific heat of zinc in the range 1·2 to 4·2° K. The linearity of the graph C_v/T *versus* T^2 below 3° K. indicates the validity of the equation $C_v = aT + bT^3$. By evaluating '*a*' and '*b*' it is found that

$$C_v \text{ (zinc)} = [(1{\cdot}630 \pm 0{\cdot}046)\,T + (0{\cdot}143 \pm 0{\cdot}009)\,T^3]\,10^{-4} \text{ Cal./° K.}$$

This result is compared with those of earlier workers in Table I.

TABLE I

	Purity %	$a \times 10^4$	θ° K.
This work ..	99·95	1·630	319
Keesom and Van den Ende ..		..	200–300
	Burton[1] (1940)	1·55	320
	Silvidi and Daunt[2]	1·25	..
Silvidi and Daunt ..	99·9	1·50	291
Daunt and Heer (below 1° K.) ..		1·36	..

[1] Value derived by Burton from the specific heat data of Keesom and Van den Ende.

[2] Value derived by Silvidi and Daunt from the specific heat data of Keesom and Van den Ende.

From Table I it is noticed that the value of the electronic specific heat constant of the present work compare well with the calorimetric data of Keesom and Van den Ende (1932) as calculated by Burton (1940) and also with that of Silvidi and Daunt (1950).

Figure 1 (*b*) shows the variation of the specific heat of cadmium with temperature in the liquid helium range. For this metal C_v/T *versus* T^2 is found to be linear below 2·5° K. By the application of the method of least

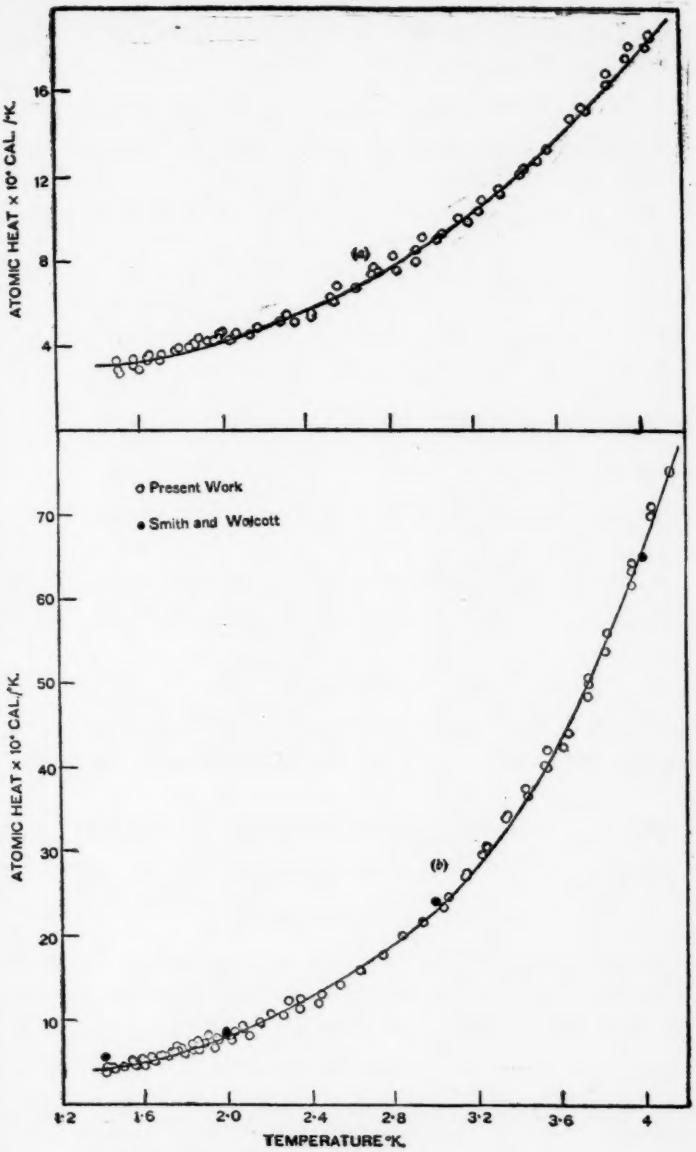

FIG. 1. (*a*) Variation of Atomic Heat of Zinc.
(*b*) Variation of Atomic Heat of Cadmium.

squares to all the points below 2·5° K., the electronic specific heat constant is found to be $1{\cdot}518 \times 10^{-4}$ and the Debye θ value to be 189° K. The specific heat equation of cadmium is then written as

$$C_v \text{ (cadmium)} = [(1{\cdot}518 \pm 0{\cdot}138)\,T + (0{\cdot}689 \pm 0{\cdot}040)\,T^3]\,10^{-4} \text{ Cal./° K.}$$

A comparison of the various results is given in Table II.

TABLE II

	Purity %	$a \times 10^4$	θ° K.
This work ..	99·95	1·158	189
Smith and Wolcott ..	99·99	1·50	188
Goodman and Mendoza (below 1° K.) ..	..	1·28	..
Samoilov (below 1° K.) ..	..	1·70	..
Smith and Daunt (below 1° K.) ..	..	1·54	..

The Debye θ value and the electronic specific heat constant of the present work agree well with the calorimetric values of Smith and Wolcott (1956).

SUMMARY

The specific heats of zinc and cadmium have been measured at liquid helium temperatures (4·2 to 1·3° K.) and are found to be represented by the formula

$$C_v \text{ (zinc)} = 10^{-4}\,[(1{\cdot}630 \pm 0{\cdot}046)\,T + (0{\cdot}143 \pm 0{\cdot}009)\,T^3] \text{ Cal./° K.}$$

$$C_v \text{ (cadmium)} = 10^{-4}\,[(1{\cdot}518 \pm 0{\cdot}138)\,T + (0{\cdot}689 \pm 0{\cdot}040)\,T^3] \text{ Cal./° K.}$$

ACKNOWLEDGEMENTS

The author is very grateful to Dr. K. G. Ramanathan for his guidance throughout the course of this investigation. He also thanks Sir K. S. Krishnan, F.R.S., for his kind interest in this work.

REFERENCES

Burton, E. F., Grayson Smith, H. and Wilhelm, J. O. — *Phenomena at the Temperature of Liquid Helium* (Reinhold Publishing Corporation, New York), 1940, p. 348.

Craig, R. S. *et al.* .. — *J. Amer. Chem. Soc.*, 1954, **76**, 238.

Daunt, J. G. and Heer, C. V. .. — *Phy. Rev.*, 1949, **76**, 1324.

Goodman, B. B. and Mendoza, E.	*Phil. Mag.*, 1951, **42,** 594.
Keesom, W. H. and Van den Ende, J. N.	*Proc. Roy. Acad. Amsterdam*, 1932, **35,** 143; Leiden Comm. No. 219 (*b*).
Ramanathan, K. G. and Srinivasan, T. M.	*Phil. Mag.*, 1955, **46,** 338.
Samoilov, B. N. ..	*Dokl. Akad. Nauk., S.S.S.R.*, 1952, **86** (2), 281.
Silvidi, A. A. and Daunt, J. G.	*Phys. Rev.*, 1950, **77,** 125.
Simon, F. E. and Lange, F. ..	*Z. Phys. Chem.*, 1928, **134,** 374.
Smith, P. L. and Wolcott, N. M.	*Phil. Mag.*, 1956, **1,** 854.
Smith, T. S. and Daunt, J. G. ..	*Phys. Rev.*, 1952, **88,** 1172.
Van Dijk, H. and Shoenberg, D.	*Nature*, 1949, **164,** 151.

DISCRETE SYMMETRIES AND CHIRALITY INVARIANCE IN QUANTUM FIELD DYNAMICS

By E. C. G. Sudarshan

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Received October 7, 1958

(Communicated by Dr. A. Ramakrishnan, F.A.SC.)

Abstract

The aim of the present paper is to discuss systematically the discrete symmetry operations on a quantized field in interaction; and to base the introduction of the new quantum number "chirality" for spinor fields on these symmetry properties. In the course of this investigation, several general results on the group of symmetry operations are proved and relation between certain sets of discrete symmetry operations and the spinor representation of the rotation group in 3 and 4 dimensions is established. An attempt has been made to present clearly the connection between additive and multiplicative quantum numbers, gauge transformations, unitary transformations and invariance laws. The chirality invariance of spinor fields in interaction is discussed in some detail. The emphasis throughout is on the systematic development rather than on details of application. The paper is divided into two parts, the first dealing with the general theory of discrete symmetry operations and the second concerned with chirality invariance for spinor fields.

I. General Principles

(1) *Additive and Multiplicative Operators.*—We wish to discuss briefly the two types of quantum numbers associated with symmetry operations. On the one hand, we have unitary operators U acting on many particle states yielding an eigenvalue which is the product of the eigenvalues of the corresponding operator acting on the single particle states from which the many particle states may be supposed to be constituted. For example, since

$$U a_r^* a_s^* \mid 0\rangle = U\, a_r^*\, U^{-1}\, U a_s^*\, U^{-1}\, U \mid 0\rangle$$

introducing the eigenvalues λ_{rs}, λ_r, λ_s

$$U a_r^* a_s^* \mid 0\rangle = \lambda_{rs} a_r^* a_s^* \mid 0\rangle \; U a_r^* \mid 0\rangle = \lambda_r a_r^* \mid 0\rangle,$$
$$U a_s^* \mid 0\rangle = \lambda_s a_s^* \mid 0\rangle,$$

one has the multiplicative relation

$$\lambda_{rs} = \lambda_r \lambda_s.$$

On the other hand, additive quantum numbers like the number operator $N = \sum_n \alpha_n^* \alpha_n$ has eigenvalues N_{rs}, N_r, N_s which satisfy the additive relation

$$N_{rs} = N_r + N_s.$$

It is the latter group of operators which illustrate most directly the particle properties of a quantised field; and the familiar dynamical quantities like energy momentum and electric charge all belong to this class.

In practice, the multiplicative operators of physical significance are always unitary and hence have eigenvalues of modulus unity. While in general all unimodular eigenvalues are permissible, we shall find it convenient to confine our attention at the outset to those cases where $U^2 = +1$. Here we point out an important elementary connection between such multiplicative unitary operators and additive operators with integral eigenvalues.

Operating on one particle states the eigenvalues of operators U are always ± 1 and may hence be replaced by a matrix w with eigenvalues ± 1. Since the transformation is unitary, it maps creation operators into creation operators and we restrict ourselves to those cases where the mapping takes one particle states into one particle states. One can hence always put

$$U\,|\,0\rangle = |\,0\rangle$$

without introducing any inconsistency. We note that the effect of the operator U on a product of field operators A.B.C. .....is given by the rule:

$$A \rightarrow UAU^{-1} = (wA)$$

$$A.B.C..... \rightarrow UAU^{-1}.UBU^{-1}.UCU^{-1}....$$

$$(wA)\,(wB)\,(wC).... = \Omega_\pi A.B.C....$$

By the definition $U\,|\,0\rangle = |\,0\rangle$, acting on any state Ω_π becomes identical to U.

On the other hand, we may define an additive operator Ω_σ by the relation

$$\Omega_\sigma A.B.C.... \equiv (wA).B.C.... + A.(wB).C....$$

$$+ A.B.\,(wC).... + ...$$

Such an operator satisfies the equation

$$\Omega_\sigma A = A\Omega_\sigma + wA \quad \text{or} \quad [\Omega_\sigma, A] = wA.$$

The solution of this equation can be constructed as follows: diagonalise w. The creation operators separate into two classes corresponding to the eigenvalues ± 1. The destruction operators also possess the same eigenvalue for w as the corresponding creation operators. For every creation operator C_n^* construct the number operator $C_n^* C_n$. The additive operator Ω_σ is then defined by the relation:

$$\Omega_\sigma = \sum_n{}^{(+)} C_n^* C_n - \sum_n{}^{(-)} C_n^* C_n$$

$\Sigma^{(+)}$ running over positive eigenvalues and $\Sigma^{(-)}$ over negative eigenvalues for w. Direct calculation shows that the operator so defined satisfies the requirements imposed on it.

With suitable modification of the steps, the restriction to the eigenvalues ± 1 may be relaxed.

(2) *Discontinuous Symmetry Operations on a Spinor Field.*—The following discontinuous operations on the field operator are standard:

$$\psi_{(x)} \rightarrow U_p \psi_{(x)} U_p^{-1} = \beta\psi(-x)$$

$$\bar{\psi}_{(x)} \rightarrow \bar{\psi}(-x)\beta \qquad \text{Space reflection}$$

$$\psi_{(x)} \rightarrow U_c \psi_{(x)} U_c^{-1} = C'\psi^+_{(x)} = C\bar{\psi}^{\mathrm{T}}_{(x)} \quad \text{Charge conjugation}$$

$$\bar{\psi}_{(x)} \rightarrow \bar{\psi}^{\mathrm{T}} C'^{-1}$$

In each of these cases, U is a unitary operator acting on the Hilbert space which can be constructed explicitly. Notice that in all cases $U^2 = +1$ and hence the eigenvalues of U operating on any state are ± 1 and thus define " parities ".

Anticipating our discussion in Chapter II, we shall now introduce an additional operation valid only for a spinor field of vanishing mass:

$$\psi_{(x)} \rightarrow U_x \psi_{(x)} U_x^{-1} = \gamma_5 \psi_{(x)}$$

$$\bar{\psi}_{(x)} \rightarrow -\bar{\psi}_{(x)} \gamma_5 \qquad \text{Chiral adjoint.}$$

Again one notices that $U_x^2 = +1$ and U_x operating on a one particle state yields its chiral number. A state possessing an even (odd) number of negative chiral particles has the eigenvalue $+1$ (-1) for U_x.

(3) *The Algebra of Symmetry Operators.*—The method of replacing unitary transformation U by their associated matrix operators w gives a

convenient method of studying the group of symmetry operations. Such a group is completely defined by specifying the transformation properties of a complete set of fundamental operators (*i.e.*, the set of operators which cannot be obtained by algebraic manipulations from other operators already considered). Since the unitary transformations considered preserve adjoint relations, such a complete set is provided by the 4 sets $a_r^*(k)$, $b_r^*(k)$ $(r = 1, 2)$. The matrix operators w perform linear transformations in the vector space of the fundamental field operators $a_r^*(k)$, $b_r^*(k)$. From the definition of the symmetry transformations one has the following results:

Charge conjugation C: $a_{1,2}^*(k) \rightarrow b_{1,2}^*(k)\; b^*_{1,2}(k) \rightarrow a^*_{1,2}(k)$

Space reflection P: $a^*_{1,2}(k) \rightarrow a^*_{2,1}(-k)\; b^*_{1,2}(k) \rightarrow -b^*_{2,1}(-k)$

Chiral adjoint X: $a_2^*(k) \rightarrow -a_2^*(k)\; b_1^*(k) \rightarrow b_1^*(k)$

$$a_1^*(k) \rightarrow a_1^*(k)\; b_2^*(k) \rightarrow -b_2^*(k)$$

The corresponding unitary operators U_c, U_p, U_x can be constructed using standard methods[4,5] and yield the following expressions:

$$\begin{aligned} U_c = \prod_k \{&1 - a_1^*(k)\,a_1(k) - b_2^*(k)\,b_2(k) + a_1^*(k)\,b_2(k) \\ &+ b_2^*(k)\,a_1(k)\}\,\{1 - a_2^*(k)\,a_2(k) - b_1^*(k)\,b_1(k) \\ &+ a_2^*(k)\,b_1(k) + b_1^*(k)\,a_2(k)\}. \end{aligned}$$

$$\begin{aligned} U_p = \prod_k \{&1 - a_1^*(k)\,a_1(k) - a_2^*(k)\,a_2(k) + a_1^*(k)\,a_2(-k) \\ &+ a_2^*(-k)\,a_1(k)\}\,\{1 - b_1^*(k)\,b_1(k) \\ &- b_2^*(-k)\,b_2(-k) - b_1^*(k)\,b_2(-k) \\ &- b_2^*(-k)\,b_1(k)\}. \end{aligned}$$

$$U_x = \prod_k \{1 - 2a_2^*(k)\,a_2(k)\}\;\{1 - 2b_2^*(k)\,b_2(k)\}.$$

One can also introduce a particle adjoint by the rule:

Particle adjoint ν: $a_r^*(k) \rightarrow a_r^*(k)\; b_r^*(k) \rightarrow -b_r^*(k)$

$$U_\nu = \prod_{k,r} \{1 - 2b_r^* b_r\}.$$

Since fundamental field operators form a (closed) representation space $\mathfrak{S}$ for the non-singular operators C, P, X, ν one can consider new

transformations generated by successive applications of these. Thus we are led to the following transformations:

$$\begin{array}{lll} \mathrm{CP} & \mathrm{CX} & \mathrm{C}\nu \\ \mathrm{PX} & \mathrm{P}\nu & \mathrm{X}\nu \end{array}$$

and to products of more than two factors. In associating w_i with the U_i so generated, one has to see whether the eigenvalues, in $\mathfrak{S}$, of the product operation is real or imaginary. Thus for example

$$(\mathrm{C}\nu) \quad \mathrm{A}\,(\mathrm{C}\nu)^{-1} = iw\mathrm{A} \qquad w \text{ hermitian}$$

since the w matrices for C and ν anticommute.

By virtue of the fact that $\mathrm{U}_i^2 = +1$, the algebra generated by n operators U_i consists of $n!$ distinct elements in general. However since the one particle submatrices for G, C, P, X, ν either commute or anticommute so that in $\mathfrak{S}$ the number of distinct matrices one has to consider is reduced to

$$n + \frac{n\,(n-1)}{2\,!} + \ldots . = 2^n - 1.$$

The following comments are generally valid:

(*i*) The hermitian w_i have the composition property

$$w_{\mathrm{R}_1} w_{\mathrm{R}_2} = k w_{\mathrm{R}_1} w_{\mathrm{R}_2}$$

where $k = +1$ if R_1 and R_2 commute and $k = -i$ if they anticommute (operating on $\mathfrak{S}$).

(*ii*) Any algebraically independent subset $\mathrm{R}_1, \mathrm{R}_2, \ldots, \mathrm{R}_h$ generates a subgroup of order 2^h including the identity.

(*iii*) In particular, any two elements R_1, R_2 generate a group of order 4 which is isomorphic to the Abelian group generated by σ_3 and -1 if R_1, R_2 commute and isomorphic to the Pauli group generated by σ_1, σ_2 if R_1, R_2 anticommute.

The introduction of the hermitian w_i enables us to define the additive quantum numbers Ω_{σ_i} associated with U_i. The following correspondences may be directly verified:

$\mathrm{X} \leftrightarrow$ total chiral number

$\nu \leftrightarrow$ Number of particle—number of antiparticles.

P ↔ Number of positive parity particles—Number of negative parity particles.

(4) *Conjugate Symmetry Operations.*—For a pair of anticommuting operations R, S the associated hermitian matrices obey the law of composition:

$$w_{RS} = - w_R w_S.$$

We shall say that such a pair of R and S are " conjugate " operations.[6] Examples are (C, ν), (C, $iC\nu$), (P, X), etc. One recalls that the $\mathfrak{S}$ matrices w_R, w_S, w_{RS} are isomorphic to the Pauli matrices σ_1, σ_2, σ_3. We shall now prove the following;

LEMMA I.—Under each transformation of a conjugate pair of symmetry operators, the 4 sets of field operators $a_r^*(k)$, $b_r^*(k)$ are spanned by two equal groups (of vectors in $\mathfrak{S}$) one corresponding to the eigenvalue $+1$ and the other to -1.

The proof is immediate if one diagonalises the corresponding hermitian w_R. Since $U_R^2 \neq +1$, $w_R^2 = +1$ and hence its eigenvalues are ± 1. But,

$$Tr\{w\}_S = Tr\{iw_{RS}w_R\} = \frac{i}{2} Tr\{w_{RS}w_R + w_R w_{RS}\} = 0$$

and hence the eigenvalues should be ± 1 in pairs.

Let the linear set in $\mathfrak{S}$ corresponding to the eigenvalue $+1$ of w be labelled η_λ ($\lambda = 1 \cdot 2$) so that

$$w_R \eta_\lambda = + \eta_\lambda.$$

It then follows that ζ_λ defined by

$$\zeta_\lambda = \omega_S \eta_\lambda$$

satisfy the relation

$$w_R \zeta_\lambda = w_R w_S \eta_\lambda = - w_S w_R \eta_\lambda = - \zeta_\lambda$$

and thus belongs to the eigenvalue -1. The operation of multiplication by w_S, which is equivalent to a unitary transformation by U_S, thus changes the sign of the eigenvalues. We thus have:

LEMMA II.—The unitary transformations U_S associated with one of a pair (R, S) of conjugate symmetry operations causes the eigensubspaces (in $\mathfrak{S}$) of the other operator to be conjugated.

This result is most familiar to us in the form in which $R = C$ and $S = \nu$, so that the particle number (" charge ") eigenstates are conjugated by the charge conjugation operator and *vice versa*.

In passing we notice that if R and S are conjugate, so are (iRS, R) and (iRS, S). Also if Q and R commute as well as Q and S, then (QR, S), (R, QS) and (QR, QS) are also conjugate pairs. This implies that, given an operator R, its conjugate S is not unique and to define S uniquely, additional requirements should be placed on it.[1]

(5) *Operator Gauge Transformations.*—Among the conserved integer-valued quantum numbers that we have considered, there are serveral which are " absolutely " conserved by any " physical " interactions. By physical, here we mean any existing interaction, however weak, consistent with our present knowledge. In such a case the states with different values of this number are physically disjoint and the well-known irrelevance of the absolute phase factor of state vectors gets extended into an arbitrary phase assignment for each of the orthogonal subspaces of the Hilbert space referring to different values for the absolutely conserved quantum number considered.[7] This corresponds to a unitary transformation in the Hilbert space of states and an associated unitary transformation on the field operators which leaves the physical content of the theory unaltered. In case the field operators have matrix elements connecting these different orthogonal subspaces (and are, by definition, not observables), this unitary transformation leads to an operator gauge transformation of the field operators. We turn to a few special cases of the same.

Consider a familiar case: as far as we know, the electric charge Q is conserved absolutely. Hence different eigensubspaces of Q are physically disjoint. Hence the phase transformation

$$| Q\rangle \rightarrow \exp.\{i\lambda(Q)\} \, | Q\rangle$$

where $\lambda(Q)$ is a (numerical-valued) function of the operator Q, leaves physical predictions unaltered. On the operators ψ this lead to the operator gauge transformation

$$\psi \rightarrow e^{i\lambda(Q)} \psi e^{-i\lambda(Q)} = e^{i\{\lambda(Q)-\lambda(Q+q)\}} \psi$$

where

$$[\psi, Q] = q\psi \qquad q = \pm 1, 0$$

For the particular choice

$$\lambda(Q) = \lambda \, . \, Q$$

λ being a c-number, the operator gauge transformation degenerates into a familiar c-number gauge transformation of the first kind:

$$\psi \rightarrow e^{-i\lambda q_\sigma}\psi.$$

Similar results hold for other absolutely conserved operators.

The same concepts are applicable to the symmetry operators and related additive operators Ω_σ. Consider for example, the one particle eigenstates of chirality. If the total Lagrangian absolutely conserves chirality, there is no way of measuring the relative phase factors of the different eigenstates and there is an essential arbitrariness of these phase factors. The chiral conjugation operator is also arbitrary then to the extent that interchanging states of opposite chirality with fixed (but arbitrary) phase factors is its generic function. A phase transformation of the type discussed above on the Hilbert space would then induce associated rotations of the chiral conjugation operator (in the abstract 3-space of the Pauli group generated by these conjugate operators).

(6) *Continuous Transformation Generated by Discrete Operators.*—The gauge transformations resulting from a conserved discrete operator form a continuous group with the discrete operator acting as a generator. It is the aim of this section to exploit this connection and develop the relation of (discrete) conjugate symmetry operators to a continuous rotation group.

Consider the rotation group in a 3-dimensional space and an arbitrary representation by matrices S_1, S_2, S_3 of the infinitesimal generators of rotations about 3 arbitrarily chosen (orthogonal) axes. Then the reflection operators are distinct from the spin operators S_i in all cases except for spin $\frac{1}{2}$. In this unique case, the reflection and spin operators are identical. This circumstance of the basic spinor rotation operators representing reflections is fundamental in the geometric theory of spinors.

Given a 2-component spinor

$$\xi = \begin{pmatrix} \xi_1 \\ \xi_2 \end{pmatrix},$$

the reflection with respect to a plane normal to the unit vector n is defined by the linear transformation[8]:

$$\begin{pmatrix} \xi_1 \\ \xi_2 \end{pmatrix} \rightarrow \begin{pmatrix} n_3 & n_1 - in_2 \\ n_1 + in_2 & -n_3 \end{pmatrix} \begin{pmatrix} \xi_1 \\ \xi_2 \end{pmatrix} \quad \text{or} \quad \xi \rightarrow \sigma.n\,\xi.$$

The rotation around the axis n through an angle θ can be generated by two successive reflections in planes passing through n and inclined at an angle

$\theta|2$. The matrix operators σ thus play a dual role. Any representation of all three reflection operators automatically leads to a representation of the continuous rotation group. This property is shared by no other representation and singles out the fundamental spinor representation of the rotation group.

The discrete symmetry operations which we have considered so far have the property that they have only two distinct eigenvalues ± 1. They consequently admit a 2-component representation. We know, further, that two conjugate symmetry operations generate a group isomorphic to the Pauli group. In view of the above identification of the rotation and reflection operations for two component representations, we are led to assert that any two conjugate symmetry operations generate a group of continuous rotations in an abstract 3-dimensional space and yield a spinor representation of this group.

Take for example charge conjugation (C) and chirality (X). Call the operator iCX by Y. The creation operators of a positive chiral eigenstate a^* and its antiparticle b^* (of automatically the opposite chirality), or equivalently, the one particle states $a^* \mid 0\rangle \equiv \mid \mathrm{A}\rangle$, $b^* \mid 0\rangle \equiv \mid \mathrm{B}\rangle$, yield the following representation for C, Y, X:

$$\mathrm{C}\begin{pmatrix} \mid \mathrm{A}\rangle \\ \mid \mathrm{B}\rangle \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} \mid \mathrm{A}\rangle \\ \mid \mathrm{B}\rangle \end{pmatrix} \qquad \mathrm{Y}\begin{pmatrix} \mid \mathrm{A}\rangle \\ \mid \mathrm{B}\rangle \end{pmatrix} = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} \mid \mathrm{A}\rangle \\ \mid \mathrm{B}\rangle \end{pmatrix}$$

$$\mathrm{X}\begin{pmatrix} \mid \mathrm{A}\rangle \\ \mid \mathrm{B}\rangle \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} \mid \mathrm{A}\rangle \\ \mid \mathrm{B}\rangle \end{pmatrix}.$$

If n is a unit vector the operations

$$\begin{pmatrix} \mid \mathrm{A}\rangle \\ \mid \mathrm{B}\rangle \end{pmatrix} \to \begin{pmatrix} n_3 & n_1 - in_2 \\ n_{1+in_2} & -n_3 \end{pmatrix}\begin{pmatrix} \mid \mathrm{A}\rangle \\ \mid \mathrm{B}\rangle \end{pmatrix} = (n_1\mathrm{C} + n_2\mathrm{Y} + n_3\mathrm{X})\begin{pmatrix} \mid \mathrm{A}\rangle \\ \mid \mathrm{B}\rangle \end{pmatrix}$$

form the group of rotations of the states in this abstract space.

A related group has been discussed by Gursey[9] where one chooses ν, C, iCν to be the three operators generating the rotation group. They identify the structure of this group with that of the internal symmetry associated with the isotopic spin. We wish to re-emphasize here that the distinction between reflection operations and internal rotation symmetries of spin $\frac{1}{2}$ is one of terminology only.

(7) *Three- and Four-Dimensional Rotation Groups.*—From the earlier sections it is quite clear that one can construct as many 3-dimensional rotation groups as there are algebraically independent pair

of conjugate symmetry operations. The structure of the rotation group in the distinct 3-dimensional spaces constitute the complete geometrical group of rotations and reflections in a 4-dimensional space. From each distinct couple of algebraically independent pairs of conjugate operations, one can construct a 4-dimensional rotation group. In the language of the theory of group representations, the direct product of two spinor representations is equivalent to the direct-sum of two spinor representations.

The most familiar example of this type is the composition of the spatial rotation group σ with the group generated by P and X. This was employed by Dirac[10] in the construction of the γ matrices in the following form:

$$\sigma = (\sigma_1, \sigma_2, \sigma_3) \quad \rho = (\rho_1, \rho_2, \rho_3)$$

$$\rho_3 = \mathrm{X} \quad \rho_1 = \mathrm{P} \quad \rho_2 = i\mathrm{PX} \quad i.e., \quad \rho_1 = \beta, \quad \rho_2 = i\beta\gamma_5, \quad \rho_3 = \gamma_5.$$

In terms of these the vector matrices (corresponding to reflection operators) assume the form:

$$\gamma^1 = \rho_3\sigma_1 \qquad \gamma^2 = \rho_3\sigma_2 \qquad \gamma^3 = \rho_3\sigma_3 \qquad \gamma^4 = \rho_1$$

where, for convenience, we have constructed the matrices applicable to a Euclidean space (all γ^μ hermitian) rather than for a Lorentz space.[8] A similar method has been employed by Schwinger in his formulation of a 4-dimensional internal symmetry group.

In our case such a group can be constructed, for example, by choosing

$$\sigma = (\nu, \mathrm{CP}, i\mathrm{CP}\nu) \qquad \rho = (\mathrm{X}, i\mathrm{XP}, \mathrm{P}).$$

The four vector matrices are:

$$\gamma^1 = \mathrm{P}\nu \quad \gamma^2 = \mathrm{C} \quad \gamma^3 = i\mathrm{C}\nu \quad \gamma^4 = \mathrm{X}$$

with corresponding rotation operators

$$\sigma^{12} = i\mathrm{CP}\nu \qquad \sigma^{23} = \nu \qquad \sigma^{31} = \mathrm{CP}$$

$$\sigma^{34} = \mathrm{CX}\nu \qquad \sigma^{14} = i\mathrm{XP}\nu \qquad \sigma^{42} = i\mathrm{CX}$$

and the set of disjoint operators $\sigma^{\pm}$

$$\sigma_+^{\,1} = \tfrac{1}{2}\nu(1+i\mathrm{XP}) \quad \sigma_+^{\,2} = \tfrac{1}{2}\mathrm{C}(\mathrm{P}+i\mathrm{X}) \quad \sigma_+^{\,3} = \tfrac{1}{2}\mathrm{C}\nu(\mathrm{X}+i\mathrm{P})$$

$$\sigma_-^{\,1} = \tfrac{1}{2}\nu(1-i\mathrm{XP}) \quad \sigma^{-2} = \tfrac{1}{2}\mathrm{C}(\mathrm{P}-i\mathrm{X}) \quad \sigma_-^{\,3} = \tfrac{1}{2}\mathrm{C}\nu(-\mathrm{X}+i\mathrm{P})$$

from independent rotations.

A physically more interesting case is got by combining a natural 3-dimensional rotation group with a set of independent conjugate symmetry operations. Such a group is generated by combining the isotopic spin symmetry with the operations X and P. We put

$$\sigma = (\tau_1, \tau_2, \tau_3) \qquad \rho = (i\mathrm{PX}, \mathrm{X}, \mathrm{P}).$$

The four vector matrices and rotation operators are

$$\gamma^1 = \mathrm{P}\tau_1 \quad \gamma^2 = \mathrm{P}\tau_2 \quad \gamma^3 = \mathrm{P}\tau_3 \quad \gamma^4 = i\mathrm{PX}$$

and

$$\sigma^{23} = \tau_1 \qquad \sigma^{31} = \tau_2 \qquad \sigma^{12} = \tau_3$$
$$\sigma^{14} = \tau_1\mathrm{X} \qquad \sigma^{42} = \tau_2\mathrm{X} \qquad \sigma^{34} = \tau_3\mathrm{X}.$$

The rotation operators thus correspond to ordinary and chiral isotopic rotations. The independent rotations are:

$$\sigma_\pm{}^1 = \tfrac{1}{2}(1 \pm \gamma_5)\,\tau_1, \quad \sigma_\pm{}^2 = \tfrac{1}{2}(1 \pm \gamma_5)\,\tau_2, \quad \sigma_\pm{}^3 = \tfrac{1}{2}(1 \pm \gamma_5)\,\tau_3$$

and thus correspond to the rotation of either chiral state separately. This case exhibits the decomposition of the direct product into a direct sum most clearly.

II. Chirality Invariance in Spinor Field Dynamics

(1) *Structure of Spinor Field Dynamics and Chirality Invariance.*—The field theory of elementary particles is patterned after the dynamics of systems with a finite number of degrees of freedom and, likewise, can be given a systematic development based on the fundamental action principle. Naturally the enumeration of the independent degrees of freedom, *i.e.*, the kinematic characterization of the dynamical system, should in turn decide the *structure* of its equations of motion, though the actual *temporal development* depends on the details of the *dynamics*. In a covariant field theory, where space and time derivatives appear on an equal footing, this intrinsic property of dynamical systems is nevertheless preserved. The complete specification of the system is contained in the action principle; and this in particular implies the generators of changes in the field operators and, from these, the commutation relations.[11]

The spinor field is the simplest dynamical system from this view-point in the sense that all the field components are independent dynamical variables. In the present paper we shall be mainly concerned with the chiral sym-

metry of spinor fields and a natural starting point for a systematic development of this is to write down the Lagrangian density:

$$\mathrm{L}(x) = \tfrac{1}{2}[\psi^*,\ i\beta\gamma^\mu\partial_\mu\psi] + \mathrm{H}(\psi)$$

where $\mathrm{H}(\psi)$ does not involve any derivatives of ψ and is called the dynamical term. The generator of changes in the field operators is

$$\mathrm{G}_\psi = i\int d^3x\psi^*_{(x)}\,\delta\psi_{(x)} \qquad [\psi_{(x)},\ \mathrm{G}_\psi] = i\delta\psi_{(x)}$$

and, consequently, the commutation relations assume the form

$$\{\psi^*_{(x)},\ \psi_{(x)}{}'\}_+ = \delta^{(3)}(x - x').$$

It is to be explicitly noticed that these commutation relations *do not* depend upon the structure of $\mathrm{H}(\psi)$ as long as no derivatives of ψ are involved in $\mathrm{H}(\psi)$. We have taken ψ to be non-hermitian and hence we have 2×4 independent sets of dynamical variables and consequently, for each value of x, 4 independent degrees of freedom.

We now notice that the two projection operators

$$\frac{1 \pm \gamma_5}{2}$$

have the property of preserving adjoint relations and lead to uncoupled degrees of freedom, when operating on the field operators ψ, ψ^*. Define:

$$\psi_\pm(x) = \frac{1 \pm \gamma_5}{2}\psi(x) \qquad \psi_\pm{}^*(x) = \psi^*(x)\frac{1 \pm \gamma_5}{2}.$$

Then the adjoint relations and commutation relations become:

$$\psi_\pm{}^* = (\psi_\pm)^* \qquad \{\psi_\pm{}^*(x),\ \psi_\mp(x')\}_+ = 0.$$

$$\{\psi_\pm{}^*(x),\ \psi_\pm(x')\}_+ = \delta^{(3)}(x - x')$$

where, as above, we have suppressed the indices. We shall call $\psi_\pm$ as the two *chiral* fields and, by convention, call ψ_+ the positive (and ψ_- the negative) chiral field.[3, 6] This possibility of exhibiting the two degrees of freedom separately is closely connected with the *Chirality invariance* of the kinematic part

$$\mathrm{L}_{kin} = \tfrac{1}{2}[\psi^*,\ i\beta\gamma^\mu\partial_\mu\psi]$$

of the Lagrangian. By this we mean that the chiral transformation

$$\psi_{(x)} \rightarrow \gamma_5\psi_{(x)} \qquad \psi^*_{(x)} \rightarrow (\gamma_5\psi_{(x)})^* = \psi^*_{(x)}\,\gamma_5$$

of the field operator ψ, leaves L_{kin} invariant. It is essential to recognize, that no specific assumption about the invariance of $H(\psi)$ has been made so far. The structure of the kinematic term alone makes it legitimate to talk about the chiral label (just like the spin label) though before it can be identified with a quantum number, the properties of the dynamical term $H(\psi)$ must be ascertained.

In fact, the kinematic independence of the chiral degrees of freedom ceases to be a dynamic independence if $H(\psi)$ is not invariant under the chiral transformation, the two chiral modes become coupled in such a case. The best example is the mass term $\frac{1}{2}m[\psi^*, \beta\psi]$. Consequently, to identify the quantum number associated with the kinematic independence, it is necessary to take a system where it becomes a dynamic independence, *i.e.*, one in which $H(\psi) = H(\gamma_5\psi)$. A trivial case of this type is got by putting $H(\psi) = 0$ obtaining a spinor field with zero mass. In this case the *conserved quantum number* associated with chirality invariance is simply the sign of the polarisation in the direction of its momentum (sometimes called " helicity "). But we employ the term chirality in its fundamental dynamical significance as a covariant label for two classes of independent modes, even in those cases where the corresponding quantum number is not conserved. Thus chirality invariance and chiral transformation are concepts independent of whether or not the corresponding quantum number is conserved or not.

In fact, it is meaningful to consider the kinematic part alone as the " free field " Lagrangian and consider all the rest to be interactions. The mass terms in $H(\psi)$ would then become a " true " interaction: and the free field would correspond to quanta of zero mass. Such a separation into " free " and " interaction " parts is best suited for discussions of chirality invariance; and is not inconsistent with the point of view that the " mass " is the phenomenological expression for the modification of space-time behaviour at very short separations.

The linear transformation of the field operator which we have called the chiral transformation can be generated by a unitary transformation on the field operator. The interaction representation corresponding to the above-discussed separation into free and interaction parts L_{kin} and $H(\psi)$ respectively permits one to write down this unitary operator U_x:

$$U_x = \pi_k \{1 - 2a_2^*(k)\, a_2(k)\}\, \{1 - 2b_1^*(k)\, b_1(k)\}.$$

Here the a_r, b_r, a_r^*, b_r^* are creation and destruction operators satisfying usual commutation rules in terms of which the field operators may be expanded:

$$\{a_r,\ a_s^*\}_+ = \delta_{rs};\quad \{b_r,\ b_s^*\}_+ = \delta_{rs};$$

all other anticommutators $= 0$

$$\psi_+ = \sum_k \{a_1(k)\, u_1(k)\, e^{ikx} + b_1^*(k)\, v_1(k)\, e^{-ik.x}\}$$

$$\psi_- = \sum_k \{a_2(k)\, u_2(k)\, e^{ikx} + b^*{}_2(k)\, v_2(k)\, e^{-ik.x}\}.$$

Notice that the labels 1, 2 here refer to chiral eigenstates (and not to spin eigenstates). To verify that the expression for U_x is the correct one, one simply writes down the relations:

$$\gamma_5 u_1(k) = +\, u_1(k) \qquad \gamma_5 v_1(k) = -\, v_1(k)$$

$$\gamma_5 u_2(k) = -\, u_2(k) \qquad \gamma_5 v_2(k) = +\, v_2(k),$$

and recognises that

$$U_x a_1 U_x^{-1} = +\, a_1 \qquad U_x b_1 U_x^{-1} = -\, b_1$$

$$U_x a_2 U_x^{-1} = -\, a_2 \qquad U_x b_2 U_x^{-1} = +\, b_2.$$

In passing we also notice the result:

$$U_x H(\psi) U_x^{-1} = H(\gamma_5 \psi).$$

It is instructive to write down the expressions for a few related operators in this representation. The familiar space reflection operation (parity) has the corresponding unitary operator $U_p{}^{el}$:

$$\begin{aligned} U_p{}^{el} = \prod_k \{&1 - a_1^*(k)\, a_1(k) - a_2^*(-k)\, a_2(-k) \\ &+ a_1^*(k)\, a_2(-k) + a_2^*(-k)\, a_1(k)\} \\ \{&1 - b_1^*(k)\, b_1(k) - b_2^*(-k)\, b_2(-k) \\ &- b_1^*(k)\, b_2(-k) - b_2^*(-k)\, b_1(k)\}. \end{aligned}$$

We also introduce two integral valued additive operators

$$N_1 = \sum_k \{a_1^*(k)\, a_1(k) - b_1^*(k)\, b_1(k)\}$$

$$N_2 = \sum_k \{a_2^*(k)\, a_2(k) - b_2^*(k)\, b_2(k)\}$$

which represent the number operators for the positive and negative chiral modes of the field operator ψ. They are the space integrated 4th components of conserved chiral currents:

$$J_1^\mu = \tfrac{1}{2}[\psi_+^*,\ \beta\gamma^\mu\psi_+] \qquad J_2^\mu = \tfrac{1}{2}[\psi_-^*,\ \beta\gamma^\mu\psi_-].$$

Alternatively one may define the chiral current and the total current:

$$j^\mu = J_1^\mu - J_2^\mu \qquad J^\mu = J_1^\mu + J_2^\mu$$

and the operators of *chiral number* and fermion number:

$$N_x = N_1 - N_2$$
$$N = N_1 + N_2.$$

In particular the one particle state $a_r^* \mid 0\rangle$, $b_r^* \mid 0\rangle$ have the following chiral numbers:

$$N_x a_1^* \mid 0\rangle = +\, a_1^* \mid 0\rangle \qquad N_x b_1^* \mid 0\rangle = -\, b_1^* \mid 0\rangle$$
$$N_x a_2^* \mid 0\rangle = -\, a_2^* \mid 0\rangle \qquad N_x b_2^* \mid 0\rangle = +\, b_2^* \mid 0\rangle.$$

Particles and antiparticles have thus opposite chiral numbers.

The conservation (or lack of it) of these dynamical quantities would depend upon the nature of the dynamical term. Our programme in the succeeding sections is to see to what extent various interactions permit the invariance under the chiral transformation. The point of view of first looking for invariance properties of the kinematic Lagrangian and then studying the transformation properties of the dynamic term under the corresponding transformations is perfectly general and very fruitful in the systematic study of symmetry properties and conservation laws. We hope to come back to this point of view elsewhere.

(2) *Electromagnetic Interaction.*—A non-trivial example of the chirality invariance of the dynamical term is the coupling of a (zero mass) spinor field to the electromagnetic field. The interaction term is obtained by replacing ∂_μ by $-ieA_\mu$ in the kinematic Lagrangian:

$$H(\psi) = \tfrac{1}{2}eA\mu\,[\psi^*,\ \beta\gamma^\mu\psi] \qquad H(\gamma_5\psi) = U_x H(\psi)\, U_x^{-1} = H(\psi).$$

Thus chirality invariance now becomes a dynamical invariance and the associated quantum number like chiral number are constants of the motion; this is most clearly seen by rewriting $H(\psi)$ in terms of $\psi_\pm$:

$$\begin{aligned} H(\psi) &= \tfrac{1}{2}\, eA\mu\,\{[\psi_+^*,\ \beta\gamma^\mu\psi_+] + [\psi_-^*,\ \beta\gamma^\mu\psi_-]\} \\ &= \tfrac{1}{2}\, e\,\{A_0([\psi_+^*,\ \psi_+] + [\psi_-^*,\ \psi_-]) + A_k([\psi_+^*,\ \alpha^k\psi_+] \\ &\qquad + [\psi_-^*,\ \alpha^k\psi_-])\}. \end{aligned}$$

Thus ψ_+ and ψ_- act as completely independent fields and their number operators are separately conserved. Thus the electromagnetic interaction is chirality invariant, but *both* chiral components are coupled (with definite phase factors).

As is well known, the electromagnetic interaction is also space reflection (parity) invariant. The parity operation has the unitary operator U_p with the properties:

$$U_p \psi_{(x)} U_p^{-1} = \beta \psi (-x) \qquad U_p A_\mu (x) U_p^{-1} = A^\mu (-x)$$
$$g^{\mu\nu} = 1, \ -1, \ -1, \ -1$$

and since $\beta \gamma^\mu \beta = \gamma_\mu$, it follows that

$$U_p H (\psi_{(x)}) U_p^{-1} = H (\psi_{(-x)}) \qquad U_p L_{kin} (x) U_p^{-1} = L_{kin} (-x)$$

which verifies the space reflection invariance. This possibility of the same interaction being chirality and parity invariant [despite the anticommutation of the corresponding linear operators γ_5 and β, when acting on the field operator ψ] stems from the fact that one of the interactions occurs in *both* the chiral eigenstates with a definite phase factor. In fact, if the phase factor is altered or the coupling constants altered in any fashion, the space reflection invariance would be destroyed.

Another conjugate operation to chirality is the well-known charge conjugation operator. [Two symmetry operations, whose squares are the identity and whose representative matrices on the field operators anticommute, are called *conjugate operations*.] Charge-conjugation invariance expresses the basic symmetry of the theory under the interchange of positive and negative electric charges. The corresponding unitary operator in our notation is:[4, 5]

$$U_c = U_c{}^{el} . U_c{}^{ph} \qquad U_c{}^{ph} e A_\mu (x) U_c{}^{ph-1} = -e A_\mu (x)$$
$$U_c{}^{el} = \pi \{1 - a_1{}^* (k) a_1 (k) - b_2{}^* (k) b_2 (k)$$
$$+ a_1{}^* (k) b_2 (k) + b_2{}^* (k) a_1 (k)\}$$
$$\times \{1 - a_2{}^* (k) a_2 (k) - b_1{}^* (k) b_1 (k) + a_2{}^* (k) b_1 (k)$$
$$+ b_1{}^* (k) a_2 (k)\}.$$

The invariance may now be explicitly verified. But we also notice that

$$U_c a^*{}_{1,2} (k) U_c^{-1} = b_{1,2}{}^* (k) \qquad U_c b_{1,2}{}^* U_c^{-1} = a_{1,2}{}^* (k)$$

and hence under charge conjugation, the chiral numbers change sign:

$$N_x U_c \mid .. > = - U_c N_x \mid .. >.$$

Again, the possibility of invariance under the two conjugate operations follows from the fact that both the particle and antiparticle states are coupled symmetrically (for each chiral component of ψ).

Since the spinor field in interaction with the electromagnetic field possesses invariance under chirality (X), parity (P) and charge conjugation (C), it is invariant under the compound operations built from these, namely, second chirality (XP), conjugate chirality (XC), combined inversion (CP) and third chirality (CPX). The explicit construction of the unitary operators U_i can be carried out using standard methods but we shall omit further discussion of these. But suffices it to note that the electromagnetic interaction manifests a remarkable degree of symmetry.

So far, we have had no need to specify whether $A\mu$ was a quantized dynamical field, or a prescribed external field. In all cases the chiral number was a constant of motion. But if $A\mu$ is a quantized field, while leaving the chiral number unaltered, it alters the "composition" of the state and this makes itself felt in the enhancement (or damping) of chirality destroying couplings. For example, if one introduces a mass term this can be thought of as a (chirality destroying) coupling to a uniform external field of zero frequency. The amplification of this "coupling" by the electromagnetic interaction exhibits itself as an electromagnetic contribution to the mass.

(3) *V–A Fourfermion Interaction.*—Among the interactions of spinor fields which are chirality invariant, the Fourfermion interactions, which are the weakest of all elementary particle interactions, is most notable.[3] The remarkable near equality of this effective weak coupling constant in various weak interactions led several authors to postulate a Universal interaction of definite pairs of charged and neutral fields. The maximal parity violations associated with minimal chiral couplings were instrumental in bringing order into the structure of these interactions. Our present knowledge is consistent with a coupling of only the positive chiral states of the pairs of fields np, $\mu\nu$, $e\nu$ (and possibly pairs like $\wedge p$, Ξp involving strange particles). The interaction is such as to conserve the number of leptons. For a review of the experimental data and the success of the predictions of the theory, reference may be made to two earlier papers.[12]

If (A_i, B_i) refer to the various pairs of charged and neutral fields taking part in the interaction, the interaction Lagrangian has the form:

$$L_{int} = \tfrac{1}{4} G \sum_{i,j} [\bar{A}_i,\ \gamma^\mu (1 + \gamma_5) B_i]^+ [\bar{A}_j,\ \gamma_\mu (1 + \gamma_5) B_j] + h.c.$$

An alternative way of rewriting this interaction is in the form:

$$L_{int} = (\tfrac{1}{2})\, G J'_{\mu} J'^{\mu} \qquad J'_{\mu} = \tfrac{1}{2} \sum_{i} [\bar{A}_i,\ \gamma_\mu (1 + \gamma_5)\, B_i]$$

G is a coupling constant with the dimensions of (length).[2]

The following properties of this interaction can be noticed immediately. First, only one chiral eigenstate is coupled. This has the consequences of (maximal) violation of space reflection invariance [*cf.* the electromagnetic interaction] and of having for all practical purposes a neutrino with only positive chirality (and an antineutrino with only negative chirality). For other particles, the mass terms " create " negative chiral states from positive chiral states and *vice versa*, so that, for example, the electron from β-decay exhibits its full set of states. Second, since the interaction was so chosen as to be bilinear in spinor fields and their adjoints, the total fermion number, summed over all the fields, is conserved and this is unaltered even by the presence of (chirality non-conserving) mass terms in the dynamical term. (Law of Conservation of Leptons.) Third, the form we have adopted for the Fourfermion interactions leads to a self-coupling of a pair of fields with half the strength, the experimental effects, say on electron-neutrino scattering, are quite small and not inconsistent with our present knowledge. Finally, for any two pairs of fields (say $\mu\nu$, $e\nu$) the present form exhibits a symmetry on interchanging charged and neutral fields: (Equivalence of Charge-Exchange and Charge-Retention orders:)

$$[\bar{\mu},\ \gamma^\mu (1 + \gamma_5)\, \nu]^{+}\ [\bar{e},\ \gamma_\mu (1 + \gamma_5)\, \nu]$$
$$= [\bar{\nu},\ \gamma^\mu (1 + \gamma_5)\, \nu]^{+}\ [\bar{e},\ \gamma_\mu (1 + \gamma_5)\, \mu].$$

From the remark made in the earlier section regarding the connection between helicity and chirality for a " free " zero mass spinor field, we expect the neutrinos from the weak interactions to possess *negative* helicity. In the case of particles like the muon and electron which are " free " but have finite masses, the chiral number is not conserved but there will result a finite degree of polarisation [with the same sign as the chira number of the probability for zero mass case is finite and opposite otherwise *cf.* the polarisation of electrons from β-decay and muons from π-decay].

Since both the electromagnetic field and the Fourfermion interaction are chirality invariant, the conservation laws of chiral number, etc., are unaltered. From the general connection between conserved quantum number and gauge transformations, we are led to expect associated gauge

transformations under which the theory is invariant. The most general gauge transformation for the present case is

$$\psi_{(\gamma)} \rightarrow \exp.\,(i\alpha_{(\gamma)})\,\psi_{(\gamma)} \qquad \alpha_{(\gamma)} = \lambda_\gamma\,(1-\gamma_5) + \theta_1\,(1+\gamma_5) + \theta_2 q_{(\gamma)} + \theta_3 b_{(\gamma)}$$

where λ_γ, θ_1, θ_2, θ_3 are arbitrary real numbers (and λ_γ may be different for different fields). $q_{(\gamma)}$ and $b_{(\gamma)}$ are the electric charge and baryon number of the field $\psi_{(\gamma)}$. It is trivial to verify that the currents generated by the 4 parts of this gauge transformations are, respectively, the (individual) current of negative chiral particles, the (total) current of positive chiral particles, the (total) electric current and the (total) baryon current. We emphasise the fact that only the transformation $\psi_{(\gamma)} \rightarrow e^{i\lambda\gamma\,(1-\gamma_5)}.\psi$ may be applied to each field separately while all other transformations should be applied to all the fields in interaction simultaneously.

The conservation laws are maintained if vector or axial vector couplings with boson fields are included. In particular, since the chiral transformations affect only the spinor fields, only the coupling matrix (and not the structure of the boson fields[13]) is relevant. In particular, a pseudovector coupling of pseudoscalar mesons with " nucleons " of zero mass leaves the abovementioned symmetries in tact.

4. *Mesic Couplings and Internal Symmetries.*—We briefly remarked in an earlier section that chirality invariances of spinor fields coupled to boson fields depended only on the covariant structure of the dynamical (coupling) term and not on the kinematic structure of the boson field. It then follows that a spin O meson field can be coupled to the spinor field in a chirality invariant fashion. Such a coupling of the pion and nucleon fields is the pseudovector interaction:

$$\tfrac{1}{2}\,g\,[\bar{\psi},\ \gamma_5\gamma_\mu\boldsymbol{\tau}\cdot\boldsymbol{\phi}^\mu\psi] = g\,(\mathbf{J}_1{}^\mu - \mathbf{J}_2{}^\mu)\cdot\boldsymbol{\phi}_\mu$$

where $\mathbf{J}_1{}^\mu$ and $\mathbf{J}_2{}^\mu$ are the chiral isotopic spin currents. The minus sign is due to the occurrence of γ_5 in the coupling. Clearly, in spite of the isotopic spin structure, the basic chirality invariance is preserved and the number of chiral particles (summed over protons and neutrons) is conserved.* In addition, the isotopic spin symmetry leads to conservation of the *total* isotopic spin current $\mathbf{J}_1{}^\mu + \mathbf{J}_2{}^\mu$ but not of the two currents separately. However, if the pion mass is zero, the sum of the chiral current $\mathbf{J}_1{}^\mu - \mathbf{J}_2{}^\mu$ and $ig^{-1}\partial_\mu\boldsymbol{\phi}$ is conserved by virtue of the equations of motion of the pion field.

* Despite these advantages, the role of the pion as the dynamical agency defining the " nucleonic charge " no longer obtains with a pseudovector coupling.

When the pion nucleon coupling is extended to include the various baryons and mesons, similar relation hold. If one sums over the various baryons, the number of positive and negative chiral particles are conserved; as well as the total isotopic spin current.

III. Acknowledgements

This work was undertaken at the suggestion and encouragement of Professor Alladi Ramakrishnan, to whom the author is indebted for his interest and encouragement. The various ideas presented here had their origin in numerous discussions with Professor Robert Marshak and Dr. Susumu Okubo. The author is indebted to them and to Dr. A. Gamba for a critical reading of the manuscript. Discussions with Professor Julian Schwinger as well as with Drs. S. Oneda, Y. Tanikawa, W. B. Teutsch and S. Watanabe are gratefully acknowledged.

IV. References

1. Wentzel, G. .. *Quantum Theory of Fields*, Interscience Publishers, New York, 1949.
2. See, *e.g.*, Schweber, S. S. and Bethe, H. A. *Mesons and Fields*, **1**, Row Peterson and Co., New York, 1955.
3. Sudarshan, E. C. G. and Marshak, R. E. *Phys. Rev.*, 1958, **109**; *see* also reference 6.
4. Wolfenstein, Cf. L. and Ravenhalli, D. G. *Ibid.*, 1953, **88**, 279.
5. Jauch, J. M. and Rohrlich, F. *Theory of Photons and Electrons*, Addison-Wesley Publishing Co., Inc., Cambridge, 1955.
6. Watanabe, S. .. *Phys. Rev.*, 1957, **106**, 1306.
7. Wick, G. C., Wightman, A. S. and Wigner, E. P. *Ibid.*, 1952, **88**, 101.
8. Cartan, E. .. *Lecons sur la theorie des Spineurs*, Tome, 1 et 2, Herman et Cie, Paris, 1938.
9. Gursey, F. Preprint; *see* also Pauli, W., *Nuovo Cimento*, 1957, **10**, 204.
10. Dirac, P. A. M. .. *The Principles of Quantum Mechanics*, Oxford University Press, Oxford, 1935.
11. Schwinger, J. .. *Phys. Rev.*, 1951, **82**, 914.
12. Sudarshan, E. C. G. and Marshak, R. E. .. *Proceedings of the Padua-Venice Conference*, 1957; Feynman, R. P. and Gell-Mann, M., *Phys Rev.*, 1958, **109**, 193.
13. Notice that we define the chiral transformation for the spinor field only and in this we differ from Watanabe (reference 6).
14. Schwinger, J. .. Private communication.

KINETIC STUDIES IN ESTER HYDROLYSIS

Part VIII. The Alkaline Hydrolysis of Ethyl Acetate in Acetone-Water Mixtures

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In earlier parts of this series published in these *Proceedings*, the reaction in these solvent mixtures were studied over a large range of compositions. While it was clear that the reaction is an ion dipole one, certain discrepancies could not escape attention. While the trend of the reaction appeared to conform to normal expectations over the range of dielectric constants, abnormal features appeared to be unavoidable in the region of small additions of the organic solvent to water, particularly a reversal of the rate-constants in relation to the dielectric constant. A fuller study of these observations (5) appeared necessary and the present report deals with this abnormal region. A similar trend had also been noticed by Tommila and his associates, 1952.

Discussion of Results

The experimental procedure adopted in the present studies involved a control of temperature and of composition as well as of analytical procedure which by standard statistical considerations can lead one to regard a difference in activation energy (Arrhenius) of the order of 300 calories as being outside the limits of experimental error. The values of the rate constants and the Arrhenius parameters for the reaction at three different temperatures are presented in Table I below. The range in temperatures had to be restricted by the low boiling point of the organic solvent and the need for a reasonable rate of reaction consistent with the accuracy aimed at. For fuller evaluation of the position of maximum rate and the drift in the position with temperature, it will be convenient to use the graphical representation in Fig. 1.

In all cases, rate constants as well as the Arrhenius parameters tend to rise progressively for small additions of organic solvent reaching a maximum in the region where the mole fraction of the acetone is between 0·015 and 0·021. Thereafter, the apparent influence of the solvent follows the normal expectations for an ion-dipole reaction. An examination of Fig. 1 further shows that increase of temperature enhances the abnormalities while retaining the general features. An examination of the Arrhenius parameters

shows that, within the limits of experimental error, the activation energy increases linearly with the mole fraction of added acetone in the initial stages

TABLE I

All rate constants are in units of moles./litre/seconds^{-1}

Mole fraction of acetone	k_2 values			E K. Calories	$\log_{10}$ PZ
	30° C.	35° C.	40° C.		
0	0·1617	0·1862	0·2817	10·530	6·75
0·00497	0·1628	0·1929	0·2891	10·880	7·01
0·01009	0·1657	0·1974	0·2967	11·050	7·14
0·01538	0·1674	0·2053	0·3059	11·430	7·41
0·02084	0·1645	0·2018	0·3094	11·970	7·81
0·02646*	0·1589	0·1889	0·2890	11·340	7·33

* The value of the Arrhenius parameters for this solvent composition differs from the values reported in Part IV. This is partly due to the greater accuracy of temperature control as well as analytical technique.

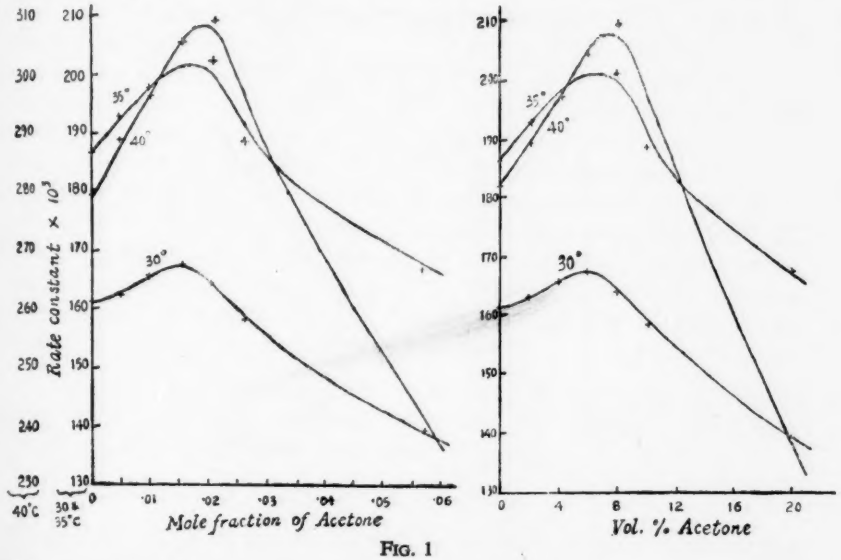


FIG. 1

before reaching a maximum value with a change in the slope thereafter (Fig. 2). The absence of any mechanistic change is clearly shown by the close parallelism between the frequency factor and Arrhenius activation energy (Fig. 3).

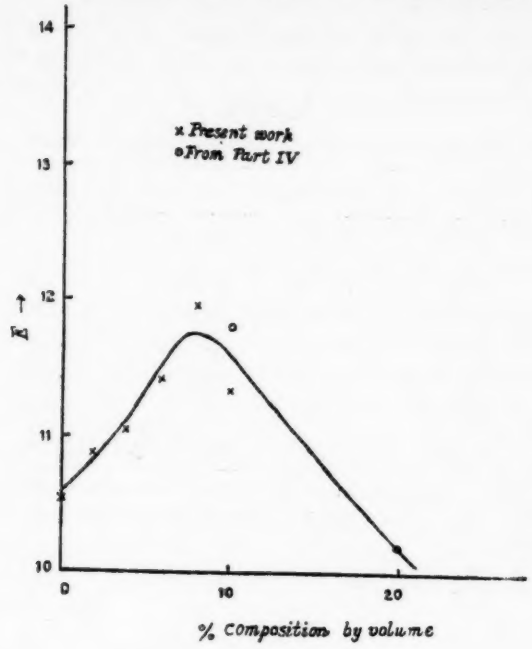

× Present work
○ From Part IV
E →
% composition by volume

FIG. 2

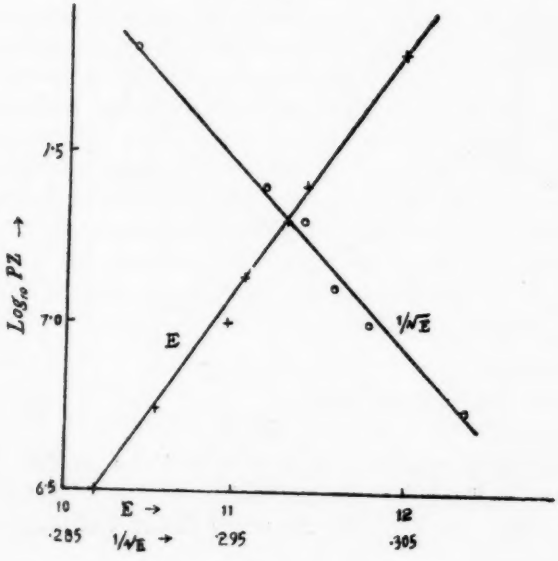

Log₁₀ PZ →
E
1/√E
E →
1/√E →

FIG. 3

A study of the physical properties of the mixtures of these two solvents clearly reveals the non-ideal behaviour of the binary system and this aspect is more fully considered in a separate communication. The last two columns of the table represent essentially composite quantities, not all of which can be readily computed. Following Fairclough and Hinshelwood (1938),[3] the entropy of activation which is included in the frequency factor of the rate equation may be considered to be related to the square-root of the activation energy and this too is noticed even where the rate constant is apparently abnormal (Fig. 3). The Arrhenius activation energy incorporates also a function of the dielectric constant of the medium but in the region of compositions used here no data are available and measurements are in progress in these laboratories to fill the gap.

Though it is generally considered that the slowest step in any postulated mechanism is the rate determining one and the measured rate constant is a measure of this part, it has to be recognised that all the terms in the rate equation are essentially composite involving all the steps. The accepted mechanism of ester hydrolysis involving hydroxyl ion catalysis involves in the first instance of a complex of the ester with the hydroxyl ion followed by interaction with solvent molecules leading to the products. Small additions of acetone can modify one or both the stages. The interacting ion is initially solvated, and as Ackermann $(1957)_1$ has shown, water molecules are disposed tetrahedrally round the hydroxylion. In the absence of evidence to the contrary, one may presume that small additions of acetone do not lead to any different reacting entity. The change in liquid structure brought about by this addition of acetone, however, alters the effective concentration of the hydrated hydroxyl ion and this should, in its turn, modify the entropy of activation. Apparently, this is balanced by the possibility of the solvation of the hydroxyl by acetone and the consequent increase in the size of the solvated ion increases the frequency of encounter.

As an ion-dipole reaction, even small changes in dielectric constant may be expected to be a dominant factor since the reaction rate constant may be ordinarily expressed by a relation of the type,

$$\ln k = \ln k_0 - f\,(1/\mathrm{D}).$$

For small additions of organic solvent, changes in dielectric constant are relatively small and the normal influence of this factor is more than offset by structural changes in the environment.

While a study of catalysis by other species was not taken up, the earlier observations of Dawson (1927)[2] together with theoretical expectations on the

role of a common ionic species made it worth while to study the influence of added potassium acetate in the different solvent mixtures. Only a single concentration was tried and an upward trend in the rate was noticeable in all cases (Table II). At the same time the position of maximum velocity in relation to solvent composition shifted to a smaller proportion of the organic solvent.

TABLE II

Influence of added potassium acetate on reaction rate

Concentration of salt: 0·0444 M

Composition of solvent: Vol. % acetone	$100\,k_2$		
	30° C.	35° C.	40° C.
0	16·42	21·42	29·14
2	17·15	22·36	30·85
4	17·33	22·79	31·41
6	16·89	21·74	29·91
8	16·37	20·62	28·90
10	15·83	19·43	28·35

The pronounced catalytic effect of acetanions as well as the increase in dielectric constant in solutions of electrolytes appear to be more important than any possible mass law effect by the presence of a common ion. There does not appear to be any trend to suggest any complications of a first order kinetics that may be expected for base catalysed alkyl-oxygen fission. Under the conditions of experiment, normal acyl-oxygen fission with a transition state involving the association of the hydroxyl ion with the ester represents the course of the kinetics.

EXPERIMENTAL

Materials used.—All the solvents used were purified by methods described in earlier parts. Conductivity water was used, freshly prepared each time. The ester was purified by standard methods and fresh samples were used for each experiment. The potassium acetate used was a Merck extra-pure quality preparation and adequate precautions had to be taken to avoid

TABLE III

(Temperature of hydrolysis: 30° C.)

Volume % Acetone	Concentration of OH'	Concentration of Ester		Titre values for 5 ml. of reaction mixture				
0	0·02634 N	0·02584 M	t sec.	92·0	271·9	477·5	751·9	1440.0
			V_t ml.	5·75	10·75	13·30	15·10	17·10
2	0·02365 N	0·02246 M	t sec.	92·4	313·0	510·8	684·1	966·1
			V_t ml.	5·90	10·85	12·95	14·15	15·30
4	0·02420 N	0·02306 M	t sec.	77·7	226·6	402·5	597·0	838·0
			V_t ml.	6·10	11·05	14·10	15·85	17·40
6	0·02400 N	0·02450 M	t sec.	83·2	257·6	456·0	679·6	1058·0
			V_t ml.	5·75	10·70	13·20	14·85	16·25
8	0·02350 N	0·02486 M	t sec.	84·0	258·7	415·6	601·2	925·2
			V_t ml.	6·10	10·90	13·10	14·60	16·05
10	0·02399 N	0·02752 M	t sec.	75·7	297·1	416·3	604·3	778·5
			V ml.	6·70	12·95	15·75	17·65	18·70

TABLE IV

(Temperature of hydrolysis: 35° C.)

Volume % Acetone	Concentration of			Titre values of aliquots				
	OH′	Ester						
0	0·02634 N	0·01981 M	t sec.	128·5	398·5	711·2	1010·0	1372·0
			V_t ml.	3·60	8·70	10·15	11·90	12·50
2	0·02665 N	0·02284 M	t sec.	94·5	358·9	593·4	891·9	1272·0
			V_t ml.	3·00	9·50	11·65	13·05	13·95
4	0·02704 N	0·02105 M	t sec.	95·2	192·4	681·9	809·8	1186·2
			V_t ml.	2·50	7·20	11·25	11·65	12·55
6	0·02770 N	0·02375 M	t sec.	97·2	326·0	664·6	1110·0	1328·0
			V_t ml.	3·00	9·10	12·15	13·40	14·05
8	0·02770 N	0·02171 M	t sec.	107·8	296·8	540·4	769·6	973·5
			V_t ml.	2·85	7·85	10·35	11·55	12·20
10	0·02704 N	0·02416 M	t sec.	118·6	380·5	639·9	908·6	1309·0
			V_t ml.	4·10	9·95	12·25	13·45	14·45

TABLE V

(Temperature of hydrolysis: 40° C.)

Volume % Acetone	Concentration of			Titre value of aliquots				
	OH′	Ester						
0	0·02845 N	0·02529 M	t sec.	86·7	275·6	465·9	836·9	1197·7
			V_t ml.	6·40	12·55	14·80	16·60	17·35
2	0·02845 N	0·02462 M	t sec.	87·90	286·7	520·7	934·3	1286·2
			V_t ml.	6·70	12·95	15·45	16·90	17·70
4	0·02715 N	0·02733 M	t sec.	80·20	278·4	475·1	763·9	1004·1
			V_t ml.	7·00	13·70	16·20	17·75	18·45
6	0·02717 N	0·02334 M	t sec.	93·20	256·5	453·6	782·3	1223·4
			V_t ml.	7·00	12·15	14·50	16·10	16·95
8	0·02629 N	0·02432 M	t sec.	78·60	248·4	424·1	675·0	883·0
			V_t ml.	6·95	13·05	15·40	16·95	17·65
10	0·02589 N	0·02305 M	t sec.	72·10	217·1	365·4	549·8	743·0
			V_t ml.	6·10	11·60	13·95	15·45	16·35

TABLE VI

The alkaline hydrolysis of ethyl acetate in the presence of potassium acetate

(Concentration of acetanions: 0·0444 M)

Volume % Acetone	Concentration of OH′	Concentration of Ester	Temp. °C.		Titre values for aliquot parts			
0	0·025656 N	0·026204 M	30	t sec.	117·3	326·1	533·0	785·2
				V_t ml.	4·85	10·25	12·65	14·40
	0·02592 N	0·02535 M	35	t sec.	107·0	319·0	506·8	793·6
				V_t ml.	5·10	10·85	13·05	14·75
	0·02627 N	0·02322 M	40	t sec.	79·90	274·00	420·3	712·0
				V_t ml.	6·70	12·50	14·20	15·80
2	0·02655 N	0·02589 M	30	t sec.	337·30	506·20	762·20	984·2
				V_t ml.	11·24	13·35	15·15	15·85
	0·02656 N	0·02246 M	35	t sec.	111·8	322·8	589·1	815·4
				V_t ml.	4·40	10·05	12·75	13·90
	0·02702 N	0·02435 M	40	t sec.	74·35	225·2	377·4	558·2
				V_t ml.	6·00	11·44	13·65	14·95
4	0·02613 N	0·02181 M	30	t sec.	276·0	503·4	693·0	999·4
				V_t ml.	8·90	11·80	13·15	14·35
	0·02526 N	0·02578 M	35	t sec.	79·4	284·7	476·4	707·6
				V_t ml.	4·50	10·90	13·20	14·65
	0·02729 N	0·02522 M	40	t sec.	87·8	261·0	443·6	747·3
				V_t ml.	6·70	11·70	13·60	15·00
6	0·02502 N	0·02578 M	30	t sec.	74·2	216·7	410·5	593·4
				V_t ml.	4·80	9·50	12·85	14·60
	0·02526 N	0·02365 M	35	t sec.	119·9	316·3	560·2	836·4
				V_t ml.	4·90	9·95	12·60	14·00
	0·02724 N	0·02609 M	40	t sec.	82·2	252·1	481·6	853·6
				V_t ml.	9·55	15·55	18·15	19·55

errors through the hygroscopic nature of the compound. The physical characteristics used conformed to the following constant values in each sample prepared:

Ethyl Acetate: B.P., 77·1–77·2° C.
n_D^{30}, 1·3690
Density$_4^{25}$, 0·9010.

Acetone: B.P., 56·1–56·2° C.
n_D^{30}, 1·3530
Density$_4^{25}$, 0·7860.

Measurements.—The reaction was carried out in tested Jena glass bottles with negligible evaporation losses at the temperatures used over several weeks. Calibrated stoppered measuring flasks were used in preparing standard solutions and in determining concentrations, corrections were applied for the expansion of the solutions. Refractive indices were determined with a Pulfrich refractometer while densities were determined with pycnometers making due allowance for buoyancy corrections. The reactions were carried out in an accurate thermostat where temperatures were electronically controlled to 0·01° C.

Aliquot parts of the reaction mixture were analysed from time to time using an electrometric titration method employing the Serfass Electron Ray Titration Unit Assembly with two platinum electrodes.

Typical runs are presented in Tables III, IV, V and VI.

In Tables III, IV and V the concentration of the acid used for chilling the reaction was about twice that of the base.

Summary

The alkaline hydrolysis of ethyl acetate in water containing small additions of acetone have shown that the earlier expectations of abnormal trend in the rate of reaction were correct. The absence of mechanistic change is indicated by the continuity in the curve for correlation of the two Arrhenius parameters. Any explanation has to be in relation to the structure of the environment of the reacting species and the requirement of the properly hydrated reacting ion.

References

1. Th. Ackermann .. *Discussions Farad. Soc.*, 1957, **24**, 180.
2. Dawson, H. M. *et al.* .. *J.C.S.*, 1927, 2444.
3. Fairclough and Hinshelwood .. *Ibid.*, 1938, 236.
4. Tommila and Hinshelwood .. *Ibid.*, 1938, 1801.
———— .. *Acad. Sci. Fennicæ*, 1952, **2 A (47)**.
5. Nair, P. M. and Anantakrishnan, S. V. *Proc. Ind. Acad. Sci.*, 1950, **32**, 187.

SEARCH FOR PHYSIOLOGICALLY ACTIVE COMPOUNDS

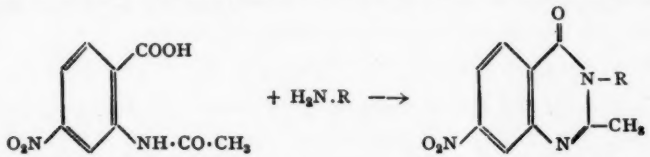
Part III. Synthesis of 7-nitro-2-methyl-3-aryl Quinazolones

By S. K. V. Seshavataram and N. V. Subba Rao, F.A.Sc.

Received October 25, 1958

Several plant materials reported to have pharmacological action contain active principles possessing quinazolone structure.[1] The mature leaves of *Glycosmis arborea* Corr., which are extensively used in Ayurvedic medicine as febrifuge and anthelminitic, were found to contain the active principle 'arborin', which is a quinazolone derivative.[2] Further, one of the three alkaloids isolated from *Glycosmis pentaphylla* (Retz) DC. was proved to have a quinazolone skeleton.[3] Since a nitro group is known to enhance the physiological properties of compounds, attempts have been made to prepare 2: 3-disubstituted quinazolones containing a nitro group para to the carbonyl in position 7.

For the synthesis of these substances, condensation of 4-nitro-N-acetyl anthranilic acid with a primary aryl amine was found to be the best method.[4]



The anthranilic acid required was prepared from *o*-toluidine by nitration followed by acetylation and oxidation with neutral potassium permanganate. By varying the aryl amine components, eight new 7-nitro-2-methyl-3-aryl quinazolones have been prepared.

The physiological activity of these compounds has been tested against two common types of bacteria, *B. coli* and *Staphylococcus aureus*. The quinazolone obtained by the condensation with *p*-bromo aniline possessed activity against *B. coli* at a concentration of one part per million, whereas most other compounds showed activity against both types of bacteria at a concentration of one part per ten thousand.

Experimental

4-Nitro-N-acetyl anthranilic acid was condensed with eight aromatic amines in toluene medium using phosphorous trichloride as the condensing agent following the procedure of Grimmel, Guenther and Morgan,[4] when

7-nitro-2-methyl-3-aryl quinazolones were obtained in good yields (above 80%). The analytical data and properties of the compounds so far not reported in literature are recorded in Table I.

TABLE I

*7-Nitro-2-methyl-3-aryl quinazolones**

No.	Amine condensed	Quinazolone obtained R =	m.p. (in °C.)	Found %			Required %		
				C	H	N	C	H	N
1.	*o*-Anisidine	*o*-Anisyl	152	61·5	4·4	13·2	61·7	4·2	13·5
2.	*o*-Toluidine	*o*-Tolyl	154	64·8	4·9	14·0	65·1	4·4	14·2
3.	*p*-Toluidine	*p*-Tolyl	223	64·8	4·7	14·0	65·1	4·4	14·2
4.	*m*-Chloro aniline	*m*-Chloro phenyl	192	57·2	3·3	13·4	57·0	3·2	13·0
5.	*p*-Bromo aniline	*p*-Bromo phenyl	>300	49·7	3·2	11·7	50·0	2·8	11·7
6.	*o*-Nitro aniline	*o*-Nitro phenyl	170	55·0	2·9	17·0	55·2	3·1	17·1
7.	*m*-Nitro aniline	*m*-Nitro phenyl	192	55·2	3·4	17·2	55·2	3·1	17·1
8.	*p*-Nitro aniline	*p*-Nitro phenyl	298	54·8	3·1	16·9	55·2	3·1	17·1

* Thanks are due to Sri. C. V. Ratnam for the analysis of the compounds.

SUMMARY

7-Nitro-2-methyl-3-aryl quinazolones have been prepared by condensation of 4-nitro-N-acetyl anthranilic acid with aryl amines. These nitro quinazolones have been tested against bacteria. The 3-(*p*-bromo phenyl) derivative is found to have the maximum activity.

REFERENCES

1. Koepfli, J. B., Mead, J. F., and Brockman, J. A. — *J. Amer. Chem. Soc.*, 1949, **71**, 1048.
2. Hutchings, B. L., Gordon, S., Ablondi, F., Wolf, C. F., and Williams, J. H. — *J. Org. Chem.*, 1952, **17**, 19.
3. Chakravarty, Mrs. D., Chakravarty, R. N., and Chakravarty, S. C. — *J. Chem. Soc.*, 1953, 3337.
4. Grimmel, H. W., Guenther, A., and Morgan, J. F. — *J. Amer. Chem. Soc.*, 1946, **68**, 542.

STUDIES ON GROUNDNUT SHELLS

Part III. The Structure of Groundnut Shell Hemicellulose B_1

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Groundnut shell hemicelluloses, which were extracted with cold 4 per cent. sodium hydroxide solution from powdered shells after a suitable pre-treatment, were resolved into six fractions using the method of O'Dwyer.[1] The chemical composition and the mode of union of the component sugars of the first fraction (A_1) have already been described in a previous paper.[2] Structural studies on the second hemicellulosic fraction (B_1) are reported in this paper.

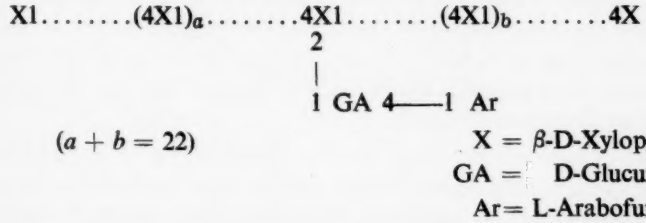
Hemicellulose B_1, which constitutes about 2 per cent. of the original material and 16 per cent. of the alkali extract, was found to contain pentosans (90·2 per cent.) and uronic acids (5·7 per cent.). Hydrolysis of the polysaccharide with dilute acid showed the presence of xylose, arabinose and glucuronic acid in the molecular ratio of 21 : 1 : 1 along with a small quantity of rhamnose, indicating that the polysaccharide is mainly composed of xylose residues. The mode of linkage of these various sugars has been inferred from a study of the hydrolytic products of the methylated hemicellulose.

Methylation was carried out with sodium hydroxide and dimethyl sulphate and was completed with silver oxide and methyl iodide. Methylated hemicellulose B_1 yielded on hydrolysis 2, 3, 4-trimethyl xylose (one mole), 2, 3, 5-trimethyl arabinose (one mole), 2, 3-dimethyl xylose (22 moles), 3-methyl xylose (one mole) and 2, 3-dimethyl glucuronic acid (one mole). Neither rhamnose nor any of its methyl ethers could be detected among the products of methanolysis. Hence, it would appear that rhamnose found among the products of preliminary hydrolysis of hemicellulose B_1 arose from an impurity.

The isolation of one molecular proportion each of 2, 3, 4-trimethyl xylose and 2, 3, 5-trimethyl arabinose suggests that these residues constitute the two end groups in this hemicellulosic fraction. Furthermore, the isolation of 3-methyl xylose indicates that this substance arises from a xylose unit linked to other residues in the molecule through positions 1, 2 and 4, thus

forming a branch point. As positions 1 and 4 are generally involved in the formation of the main chain, it may be inferred that the branching takes place through the C_2 position of the xylose residue in the main chain.

It is also significant to note that an aldobiouronic acid could not be isolated from the products of hydrolysis, as could be done during the hydrolysis of groundnut shell hemicellulose A_1. The simple uronic acid derivative isolated is 2, 3-dimethyl glucuronic acid and its formation during the hydrolysis of the fully methylated hemicellulose B_1 indicates that it is linked with the other residues through the positions 1 and 4. Bearing in mind the isolation of an aldobiouronic acid [2-0-(2, 3, 4-tri-O-methyl-D-glucuronosyl)-3-O-methyl-D-xylose] by the methanolysis of groundnut shell hemicellulose A_1 and the well-known inertness of such residues to ordinary hydrolytic procedures, it is conceivable that the isolation of a simple glucuronic acid derivative in this case is due to the greater susceptibility conferred on the aldobiouronic acid residue by the presence of other sugars on the uronic acid moiety. An arabofuranose residue is known not only to modify the solubility of hemicelluloses but also promote their susceptibility to hydrolytic reagents.[3–5] This surmise is confirmed by the isolation of 2, 3, 5-trimethyl arabinose. Hence, it appears very probable that the C_4 position of the uronic acid is attached to the 1 position of an arabinose unit. That this is so, is supported by the observation that hemicellulose B_1 after a mild treatment with oxalic acid in order to split off the arabofuranose residue does not show significant increment in its reducing power. Based on the above observation and the negative specific rotation of this hemicellulosic fraction, the following structure may be proposed for groundnut shell hemicellulose B_1:—



$(a + b = 22)$

X = β-D-Xylopyranose
GA = D-Glucuronic acid
Ar = L-Arabofuranose

It is evident from these results that the main structural feature of hemicellulose B_1 is similar to the one observed in hemicellulose A_1, the only difference being in the nature of the side-chain. Hemicellulose A_1 contains D-glucuronic acid residue existing as a side-chain through the C_2 position of a xylose residue. In hemicellulose B_1 arabinose is attached to glucuronic acid which itself is linked to the main chain of xylose residues, thus forming

a branched chain 1 GA 4—1 Ar. Such a unit has not so far been found in hemicelluloses, although its presence has been reported in gums.[6–8]

EXPERIMENTAL

Material.—Hemicellulose B_1 was prepared by adding acetone to the insoluble copper complex of hemicellulose B_1 after decomposing with glacial acetic acid (see Part I for details of the preparation).

Analysis.—The analysis of groundnut shell hemicellulose B_1 was carried out by standard methods[9] and the following results were obtained: Ash 0·74 per cent.: Lignin 1·24 per cent.: Pentosans 90·24 per cent. and Uronic acids 5·70 per cent.

Hydrolysis of the hemicellulose B_1 and the quantitative separation of the products of hydrolysis.—Hemicellulose B_1 (2·2 g.) was hydrolysed with sulphuric acid (1%; 150 ml.) at 50° C., till the optical rotation of the hydrolysate was constant. The reaction mixture was neutralised with barium carbonate, filtered and the residue was washed several times with hot water. The filtrate and the washings were added to excess of alcohol to precipitate the barium salt of the acidic component (0·17 g.).

The neutral solution obtained after removing the acidic component as the barium salt was concentrated to a syrup under reduced pressure and fractionated on a cellulose column.[10] Three fractions identified as D-xylose (1·88 g.), L-arabinose (0·088 g.) and L-rhamnose (0·013 g.) were obtained.

Identification of the acidic component.—The barium salt of the acidic component [$(\alpha)_D^{24}$ + 76·4] containing 25·8 per cent. of barium was dissolved in distilled water and deionised through a column of Amberlite IR-120. The clear eluate was concentrated under reduced pressure and dried *in vacuo*. The acid obtained had m.p. 156° C., and $(\alpha)_D^{25}$ + 11·5 → + 35·6 (Found: Eq. Wt. 188, Calc. for $C_6H_{10}O_7$: Eq. Wt. 194). Hence the acidic component was identified as D-glucuronic acid.

Methylation of hemicellulose B_1.—The hemicellulose (2 g.) was methylated six times with sodium hydroxide solution (40 per cent.) and dimethyl sulphate in an atmosphere of nitrogen. The methylated product obtained thus was methylated with methyl iodide and silver oxide, till there was no change in the methoxyl content [OMe, 42·8 per cent.; $(\alpha)_D^{25}$ − 52·6].

Hydrolysis of the methylated hemicellulose.—The methylated hemicellulose (2 g.) was heated under reflux with methanolic hydrogen chloride (2 per cent.; 60 ml.) for 12 hours (constant rotation). The solution was neutralised with silver carbonate, filtered and the filtrate concentrated under

reduced pressure to a syrup. The syrup was treated with N sulphuric acid to hydrolyse the methyl ester of the acidic component as well as the methyl glycosides. The reaction mixture was neutralised with barium carbonate and filtered. The residue was thoroughly washed with hot water, the filtrate and the washings were combined, passed through Amberlite IR-120, concentrated to a syrup and dried *in vacuo*.

Separation of the cleavage products.—The syrup (1·1 g.) containing the methyl ethers of sugars as well as the acidic component was fractionated on a cellulose column using *n*-butanol-ethanol-water (4 : 1 : 5) as the developing solvent. Four components were first obtained and all of them were found to be neutral in reaction. For the isolation of the acidic component the column was eluted with water. The components were identified by their physical characteristics as well as by the preparation of their derivatives. The identity and weights of the various components are given in Table I.

TABLE I

Cleavage products of the methylated hemicellulose B_1

Component	Weight in mg.	Identity	Moles
1	42·52	2, 3, 5-tri-O-methyl-L-arabofuranose	1
2	41·85	2, 3, 4-tri-O-methyl-D-xylose	1
3	867·22	2, 3-di-O-methyl-D-xylose	22
4	36·08	3-O-methyl-D-xylose	1
5	48·35	2, 3-di-O-methyl-D-glucuronic acid	1
		Recovery = 94%	

Identification of the components

(*a*) *Component* 1 (2, 3, 5-*tri-O-methyl-L-arabofuranose*).—The syrup failed to crystallise (Found: OMe, 46·4 per cent. Calc. for $C_8H_{16}O_5$: OMe, 48·4 per cent.). The syrup was dissolved in water (10 ml.) and treated with bromine (0·2 ml.) at room temperature for seven days and at 50 to 60° C. for six hours. The solution was freed from bromine by aeration, neutralised with silver carbonate, filtered and passed through a column of Amberlite IR-120. The eluate was concentrated *in vacuo* and the syrupy residue extracted with ether. Evaporation of the ether extract gave 2, 3, 5-tri-O-

methyl-L-arabono-γ-lactone, $(\alpha)_D^{28.5}$ − 41°. The lactone when treated with methanolic ammonia in the usual way gave 2, 3, 5-tri-O-methyl-L-arabono amide, m.p. 138° C.[11, 12] after recrystallisation from ethyl acetate-petroleum ether. Hence, component 1 was identified as 2, 3, 5-tri-O-methyl-L-arabofuranose.

(*b*) *Component* 2 (2, 3, 4-*tri-O-methyl-D-xylose*).—This component had m.p. 88° C. and $(\alpha)_D^{28.4}$ + 21° (Found: OMe, 46·7 per cent. Calc. for $C_8H_{16}O_5$: OMe, 48·4%). The anilide derived had m.p. 100° C. and $(\alpha)_D^{28.5}$ + 46°. Therefore, component 2 was identified as 2, 3, 4-tri-O-methyl-D-xylose.

(*c*) *Component* 3 (2, 3-*di-O-methyl-D-xylose*).—The syrup on nucleation with 2, 3-di-O-methyl-D-xylose gave a few crystals which had m.p. 62° C. and $(\alpha)_D^{28.4}$ + 69° → + 22° (Found: OMe, 33·8 per cent Calc. for $C_7H_{14}O_5$: OMe, 34·8 per cent.). The derived anilide had m.p. 145° C. and $(\alpha)_D^{28.5}$ +186°. Hence component 3 was identified as 2, 3-di-O-methyl-D-xylose.

(*d*) *Component* 4 (3-*O-methyl-D-xylose*).—This substance had m.p. 100° C. and $(\alpha)_D^{28.4}$ + 20° (Found: OMe, 18·2 per cent.; Calc. for $C_6H_{12}O_5$: OMe, 18·7 per cent.). The derived anilide had m.p. 137° C. Hence component 4 was characterised as 3-O-methyl-D-xylose.

(*e*) *Component* 5 (2, 3-*di-O-methyl-D-glucuronic acid*).—This syrupy substance had $(\alpha)_D^{28.4}$ + 68°. It was acidic to litmus and congo red papers (Found: OMe, 26·9 per cent. Calc. for $C_8H_{14}O_7$: OMe, 27·9 per cent.; Found Eq. Wt. 220. Calc. for $C_8H_{14}O_7$; Eq. Wt. 222).

The acidic component was esterified by refluxing it (20 mg.) with methanolic hydrogen chloride (2·5 per cent.; 30 ml.) for 8 hours. The solution was cooled, neutralised with silver carbonate, filtered and evaporated to dryness giving the methyl ester of methyl 2, 3-di-O-methyl-D-glucuronoside $(\alpha)_D^{28.5}$ + 76°.[13]

The methyl ester was completely methylated by one treatment with Purdie's reagents. The product isolated by means of acetone was boiled with methanolic hydrogen chloride (3 per cent.; 25 ml.) for 8 hours. The solution was cooled and neutralised with silver carbonate, filtered and evaporated to dryness giving a syrup having $(\alpha)_D^{28.5}$ + 85°. This syrup on treatment with methanolic ammonia gave the amide of methyl 2, 3, 4-tri-O-methyl-D-glucuronoside, m.p. 183° C. and $(\alpha)_D^{28.5}$ + 139°.[11]

The methyl ester of methyl 2, 3-di-O-methyl-D-glucuronoside (10 mg.) was heated for 5 hours at 110° C. with phenyl hydrazine (5 mg.). The reaction mixture on cooling gave the phenyl hydrazide of the methyl 2, 3-di-

O-methyl-D-glucuronoside m.p. 223° C. (after recrystallisation from acetone-ether-petroleum ether).

The original substance (component 5) was, therefore, characterised from the above observations as 2, 3-di-O-methyl D-glucuronic acid.

Summary

Groundnut shell hemicellulose B_1 has been shown to contain D-xylose, L-arabinose and D-glucuronic acid. The methylated polysaccharide gave on hydrolysis 2, 3, 5-tri-O-methyl-D-arabofuranose, 2, 3, 4-tri-O-methyl-D-xylose, 2, 3-di-O-methyl-D-xylose, 3-O-methyl-D-xylose and 2, 3-di-O-methyl-D-glucuronic acid in the molar ratio of 1 : 1 : 22 : 1 : 1. A structure is proposed for the hemicellulose which has a straight chain of *ca.* 22 1 : 4-linked β-D-xylopyranose residues with —1 GA 4—1 Ar existing as a side chain through the C_2 position of one of the xylose residues.

References

1. Radhakrishnamurty, B. and Srinivasan, V. R. *J.S.I.R.*, 1957, **16 C**, 59.
2. ——— .. *Proc. Ind. Acad. Sci.*, 1957, **46**, 53.
3. O'Sullivan, C. .. *J.C.S.* 1891, **59**, 1029.
4. Anderson, E., and Sands, L. .. *J.A.C.S.*, 1926, **48**, 3172.
5. White, E. V. .. *Ibid.*, 1947, **69**, 715.
6. Timell, T. E. and Jahn, E. C. *C.A.*, 1952, **46**, 6825.
7. Smith, F. .. *J.C.S.*, 1940, 1035.
8. ——— .. *Ibid.*, 1939, 744.
9. Dorée, C. .. *Methods of Cellulose Chemistry* (Chapman & Hall, Ltd.), 1947, 2nd Edn., Chapter XXII.
10. Hough, L., Jones, J. K. N. and Wadman, W. J. *J.C.S.*, 1949, 2511.
11. Smith, F. .. *Ibid.*, 1939, 1724.
12. Avery, J., Haworth, W. N. and Hirst, E. L. *Ibid.*, 1929, 739.
13. Smith, F. .. *Ibid.*, 1940, 1035.

CONSTITUTION OF DALBERGIN

Part V. A Further Study of 4-Phenyl Coumarins

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In earlier publications[1, 2] two important characteristics of 4-phenyl coumarins were recorded: (i) They give marked colour reactions[2] with magnesium and hydrochloric acid in alcoholic solution. In most cases there is an intermediate emerald green stage but finally it becomes deep red. The final colour has now been studied in two typical cases, 6 : 7-dihydroxy- and 7: 8-dihydroxy-4-phenyl coumarins. The products have the characteristic properties of the flavylium salts and after purification by methods familiarly used in the flavylium series, the 4-phenyl-6: 7-dihydroxy-pyrylium chloride gave a reddish brown ferric reaction whereas the 7: 8-dihydroxy compound gave a deep blue colour. Similar differences were noticed in the 2-phenyl pyrylium salts also.[3] (ii) They exhibit marked stability to boiling alkali[1] but undergo conversion into the corresponding coumarilic acids[4] when mercuric oxide is added to the boiling alkaline solution.

In order to collect more information about this group of compounds tri-substituted 4-phenyl coumarins have now been prepared. They are most conveniently obtained by adopting the method of *para*-nuclear oxidation. 4-Phenyl-5: 7-dimethoxy coumarin on oxidation with alkaline persulphate gave the 6-hydroxy product. For purposes of comparison it has also been synthesised using 2: 6-dimethoxy quinol and benzoyl acetic ester. 4-Phenyl-7 : 8-dimethoxy coumarin on similar oxidation gave the corresponding 6-hydroxy product. The hydroxy compounds gave on methylation 5: 6: 7-trimethoxy and 6: 7: 8-trimethoxy 4-phenyl coumarins and on demethylation 5: 6: 7-trihydroxy and 6: 7: 8-trihydroxy 4-phenyl coumarins. All these compounds exhibit bright colour reactions with magnesium and hydrochloric acid. In the course of the present study, calophyllolide,[5] which is an important naturally occurring 4-phenyl coumarin, was found to give a feeble pink colour. This peculiarity may be due to the presence of an acyl group in the molecule having an adverse effect. This surmise is supported by the further observation that 7-hydroxy-8-acetyl 4-phenyl coumarin[6] gives no colour and its methyl ether a feeable colour like calophyllolide. The trimethoxy compounds yielded the corresponding *o*-methoxy cinnamic acids

by the combined action of alcoholic potash and methyl sulphate. As in simpler cases these coumarins were also stable to the action of hot potash and were recovered unchanged on acidification, but in the presence of mercuric oxide they yielded the corresponding coumarilic acids in about 45–50% yield. It is significant that the alternative method of preparing the coumarilic acids by using bromine and subsequently potash does not work satisfactorily in all cases. Though it proceeded smoothly in the case of 6: 7: 8-trimethoxy-4-phenyl coumarin, it was complicated by nuclear bromination when 5: 6: 7-trimethoxy-4-phenyl coumarin was employed. It appeared that the presence of a methoxy group in the 5-position encourages nuclear bromination. This has been confirmed by doing parallel experiments with the simpler 4-phenyl-5: 7-dimethoxy coumarin where also nuclear bromination complicated the reaction. Hence it could be concluded that the mercuric oxide-alkali method is the most suitable general process for all the phenyl coumarins.

Experimental

Procedure for colour reaction

A solution of 50–100 mg. of the 4-phenyl coumarin in alcoholic hydrochloric acid was treated with magnesium powder (2–3 g.) added slowly with occasional cooling and shaking. The reaction mixture was allowed to remain for 5–10 minutes when it attained a deep red colour. It was diluted with water and extracted with isoamyl alcohol (5 c.c.). The isoamyl alcoholic solution was diluted with a large excess of petroleum ether (150 c.c.) and the pyrylium salt extracted with hydrochloric acid (1 : 1; 10 c.c.). The acidic solution was re-extracted with isoamyl alcohol (5 c.c.). and ferric reaction performed after adding excess of sodium acetate following the procedure of Robinson and Robinson.[7]

Preparation of trimethoxy and trihydroxy coumarins

4-Phenyl-6-hydroxy-7: 8-dimethoxy coumarin.—4-Phenyl-7: 8-dimethoxy coumarin[1] (5 g.) was refluxed with aqueous sodium hydroxide (5 g. in 100 c.c. water) till there was complete solution (2 hours). The solution was cooled (15–20°), stirred and treated dropwise with potassium persulphate (9 g. in 200 c.c. water) during 2 hours. After 24 hours at room temperature, the deep brown solution was acidified with dilute hydrochloric acid (Congo-red) and the unchanged product filtered off; further ether extraction removed the last traces of it. The clear brown solution was heated in a boiling water-bath with sodium sulphite (5 g.) and concentrated hydrochloric acid (100 c.c.) for half-an-hour. After cooling the solid product (2·5 g.) was filtered and crystallised from methyl alcohol yielding colourless micacious plates,

m.p. 212–13° (Found: C, 68·5; H, 4·7; $C_{17}H_{14}O_5$ requires C, 68·5; H, 4·7%). With magnesium and hydrochloric acid it gave a pink colour changing to green and finally to reddish brown.

The acetate prepared by boiling with acetic anhydride and pyridine crystallised from methanol as colourless stout rhombohedral prisms, m.p. 136–37°.

4-*Phenyl*-6: 7: 8-*trimethoxy coumarin* was prepared by refluxing the above 6-hydroxy coumarin (1 g.) in acetone (75 c.c.) with dimethyl sulphate (0·5 c.c.) and potassium carbonate (2 g.) for 4 hours. The product (0·9 g.) crystallised from methyl alcohol as colourless stout polygonal prisms, m.p. 109–10° (Found: C, 69·1; H, 5·1; $C_{18}H_{16}O_5$ requires C, 69·2; H, 5·2%). With magnesium and hydrochloric acid it gave a pink red colour which changed to green and finally deep red on standing.

4-*Phenyl*-6: 7: 8-*trihydroxy coumarin*.—4-Phenyl-6-hydroxy-7: 8-dimethoxy coumarin (1 g.) was heated with hydriodic acid (10 c.c.) in acetic anhydride (10 c.c.) for 2 hours at 140–45°. After working up in the usual way, the product crystallised from methanol as very pale yellow tiny prisms and needles, m.p. 238–39° (Found: C, 66·2; H, 3·9; $C_{15}H_{10}O_5$ requires C, 66·7; H, 3·7%). It gave a deep blue colour with alcoholic ferric chloride and with magnesium and hydrochloric acid a pink colour which changed to green and finally red.

The triacetate was prepared by heating the above product with acetic anhydride and a drop of pyridine. It crystallised from methanol as colourless needles and elongated rectangular plates, m.p. 187–88°.

4-*Phenyl*-6-*hydroxy*-5: 7-*dimethoxy coumarin*

(*a*) *Nuclear oxidation of* 4-*phenyl*-5: 7-*dimethoxy coumarin*.—4-Phenyl-5: 7-dimethoxy coumarin required for this was prepared by methylation of 4-phenyl-5: 7-dihydroxy coumarin[8] with dimethyl sulphate and potassium carbonate in acetone medium. On crystallisation from methyl alcohol it melted at 166–67°, the same as reported earlier[9] for the sample prepared by the cyclisation of O-dimethyl-phlorobenzophenone.

(*a*) 4-Phenyl-5: 7-dimethoxy coumarin (5 g.) was oxidised with potassium persulphate (9 g.) in sodium hydroxide solution (5 g. in 100 c.c. water) as in the earlier case. The product (1·5 g.) crystallised from methanol as colourless thin rhombohedral plates, m.p. 185–86° (Found: C, 68·6; H, 4·8; $C_{17}H_{14}O_5$ requires C, 68·5; H, 4·7%). With magnesium and hydrochloric acid it gave a light pink colour.

(*b*) 2: 6-Dimethoxy quinol[10] (2·5 g.) was made into a paste with benzoyl acetic ester (3 c.c.), the solution cooled in ice and concentrated sulphuric acid (10 c.c.) added gradually (1 hour) with stirring at 0°. The deep red viscous solution thus obtained was kept in a refrigerator for 24 hours and then poured into water (100 c.c.) with stirring. The pale yellow precipitate (0·5 g.) was filtered and crystallised from methanol, m.p. 185–86°, undepressed by admixture with the product obtained in experiment (*a*).

The acetate crystallised from ethyl acetate as colourless stout rectangular prisms, m.p. 153–54°.

4-*Phenyl*-5: 6: 7-*trimethoxy coumarin* was prepared by methylation of the above 6-hydroxy-coumarin (1 g.) in acetone solution. The product (1 g.) separated as colourless stout rhombic prisms from methanol, m.p. 140–41° (Found: C, 69·0; H, 5·3; $C_{18}H_{16}O_5$ requires C, 69·2; H, 5·2%). With magnesium and hydrochloric acid it gave a pink colour which changed to green and finally deep red.

4-*Phenyl*-5: 6: 7-*trihydroxy coumarin* was prepared by demethylation of 4-phenyl-6-hydroxy-5: 7-dimethoxy coumarin with hydriodic acid in acetic anhydride medium. The product crystallised from methanol as pale yellow shining small plates, m.p. 236–37° (Found: C, 66·9; H, 3·9; $C_{15}H_{10}O_5$ requires C, 66·7; H, 3·7%).

The triacetate crystallised from alcohol as colourless large rectangular plates, m.p. 184–85°.

Conversion into coumarilic acids

3-*Phenyl*-4: 6-*dimethoxy coumarone*-2-*carboxylic acid.*—4-Phenyl-5: 7-dimethoxy coumarin (2 g.) was dissolved in hot aqueous potassium hydroxide (30 c.c., 20%). The solution was diluted with water (70 c.c.) and refluxed with freshly prepared yellow mercuric oxide (15 g.) for 20 hours. The mixture was filtered, the filtrate saturated with hydrogen sulphide to remove all combined mercury as mercuric sulphide and filtered again and acidified. The acid product was purified (sodium-hydrogen carbonate) and crystallised from ethyl alcohol; colourless large rectangular plates and tablets (0·9 g.), m.p. 218–19° (Found: C, 67·8; H, 5·1; $C_{17}H_{14}O_5$ requires C, 68·4; H, 4·7%). It gave a red colour with alcoholic ferric chloride.

3-*Phenyl*-4: 6-*dimethoxy coumarone*

(i) *Mercuric chloride method.*—The above acid (0·5 g.) and mercuric chloride (1 g.) were refluxed with aqueous alcohol (75 c.c., 50%) for 10 hours. The solution was acidified with hydrochloric acid to make the strength 1%.

Alcohol was distilled off under reduced pressure and the solution extracted with ether. The ether solution was washed with aqueous sodium hydrogen carbonate and the solvent distilled. The residue (0·4 g.) crystallised from methanol as colourless micacious rectangular plates, m.p. 89–90°. Mixed m.p. with an authentic sample prepared as given in (ii) was undepressed (Found: C, 75·3; H, 5·4; $C_{16}H_{14}O_3$ requires C, 75·6; H, 5·5%).

(ii) *Copper-quinoline method.*—3-Phenyl-4: 6-dimethoxy coumarone-2-carboxylic acid (0·5 g.) was heated at 220° in quinoline (10 c.c.) with copper powder (0·4 g.) until the evolution of carbon dioxide ceased (30 min.). The cooled mixture was poured into ether, the solution filtered and washed with dilute hydrochloric acid to remove quinoline and then with aqueous sodium hydrogen carbonate and the solvent distilled off. The viscous residue (0·3 g.) crystallised from methanol, m.p. 89–90°.

2: 4: 6-*Trimethoxy-β-phenyl cinnamic acid* was prepared from 4-phenyl-5: 7-dimethoxy coumarin by the action of dimethyl sulphate and methanolic potash as was done with O-methyldalbergin.[1] It crystallised from methanol as colourless stout rectangular prisms, m.p. 201–03° (Found: C, 68·5; H, 6·1; $C_{18}H_{18}O_5$ requires C, 68·8; H, 5·8%).

3-*Phenyl*-4: 5: 6-*trimethoxy coumarone*-2-*carboxylic acid* was prepared from 4-phenyl-5: 6: 7-trimethoxy coumarin, mercuric oxide and aqueous sodium hydroxide (20 hours refluxing) as in earlier cases. It crystallised from methanol as colourless small prisms, m.p. 202–03°. Yield 42% (Found: C, 65·9; H, 5·1; $C_{18}H_{16}O_6$ requires C, 65·9; H, 4·9%). Decarboxylation of the acid either with mercuric chloride or copper and quinoline gave a low melting product (neutral) which could not be crystallised.

2: 4: 5: 6-*Tetramethoxy-β-phenyl cinnamic acid* prepared from 4-phenyl-5: 6: 7-trimethoxy coumarin by the usual method crystallised from methanol as colourless shining stout prisms, m.p. 170–71° (Found: 65·7; H, 6·1; $C_{19}H_{20}O_6$ requires C, 66·2; H, 5·9%).

3-*Phenyl*-5: 6: 7-*trimethoxy coumarone*-2-*carboxylic acid*

(i) *Action of mercuric oxide and alkali on* 4-*phenyl*-6: 7: 8-*trimethoxy coumarin.*—The reaction was carried out as in earlier cases. The product crystallised from methanol as colourless rectangular prisms, m.p. 192–93° (Found: C, 65·2; H, 4·7; $C_{18}H_{16}O_6$ requires C, 65·9; H, 4·9%). Yield 45%. Mixed m.p. with an authentic sample prepared by method (ii) was undepressed.

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(ii) 3-*Bromo*-4-*phenyl*-6: 7: 8-*trimethoxy coumarin*.—To a hot solution of 4-phenyl-6: 7: 8-trimethoxy coumarin (3·1 g.) in glacial acetic acid (20 c.c.) was added a solution of bromine in glacial acetic acid (18 c.c., 10%) with shaking (10 min.). Bromine was taken up immediately and on cooling a colourless product (2·8 g.) separated out. It crystallised from glacial acetic acid as colourless large rectangular prisms, m.p. 152–53° (Found: C, 54·9; H, 3·7; $C_{18}H_{15}O_5$ Br requires C, 55·2; H, 3·8%).

Action of alkali on the bromo coumarin.—The above bromo compound (2 g.) was refluxed with aqueous sodium hydroxide (100 c.c.; 10%) for 4 hours. The solution was cooled, the insoluble portion filtered off, and the filtrate acidified with dilute hydrochloric acid. The product was filtered and purified by means of sodium hydrogen carbonate. It crystallised from methanol, m.p. 192–93°.

Decarboxylation of the above acid either with mercuric chloride or with copper and quinoline gave an oily liquid product (neutral) which could not be crystallised.

2: 3: 4: 5-*Tetramethoxy-β-phenyl cinnamic acid* prepared from 4-phenyl-6: 7: 8-trimethoxy coumarin as in earlier cases crystallised from methanol as colourless small tiny rectangular prisms, m.p. 116–17° (Found: C, 65·8; H, 5·7; $C_{19}H_{20}O_6$ requires C, 66·2; H, 5·9%).

Summary

The two important characteristics of 4-phenyl coumarin derivatives, *i.e.*, the colour reaction with magnesium and hydrochloric acid and the transformation with alkali and mercuric oxide into coumarilic acids are shown to be characteristics of the group by the study of more members. The coloured product is somewhat similar to flavylium salts. Calophyllolide does not give marked colour reaction probably due to the presence of acyl group. Mercuric oxide-alkali method is specially convenient for the preparation of 3-phenyl coumarilic acids since the alternative bromination method does not work satisfactorily with 5-substituted coumarins.

References

1. Ahluwalia, V. K. and Seshadri T. R. .. *J. Chem. Soc.*, 1957, 970.
2. ——, Mehta, A. C. and Seshadri, T. R. *Proc. Ind. Acad. Sci.*, 1957, **45 A**, 293.
3. Ponniah, L. and Seshadri, T. R. .. *Ibid.*, 1953, **38 A**, 77.
4. Ahluwalia, V. K. Mehta, A. C. and Seshadri T. R. *Tetrahedron*, 1958, **4**, 271.

5. Potier, A. O., Buzas A. and Lederer, E. .. *Bull. Soc. Chim., France*, 1951, 577.
6. Limaye, D. B. and Joshi, M. C. .. *Rasayanam*, 1941, 226.
7. Robinson, G. M. and Robinson, R. .. *Biochem. J.*, 1931, 1687.
8. Kostanecki, V. and Weber, C. .. *Ber.*, 1893, **26**, 2906.
9. Pollak, V. .. *Monatsh.* **18**, 743.
10. Baker, W. .. *Jour. Chem. Soc.*, 1941, 663.

CATALYSED SOLVOLYSIS OF BENZYL CHLORIDE

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This paper, which deals with the kinetics of the solvolysis of benzyl chloride in aqueous ethanol, under catalysis by mercuric chloride, forms part of an investigation[1–3] on electrophilic catalysis in nucleophilic aliphatic substitution.

Results and Discussion

The kinetic results are presented in Table I.

Table I

Kinetics of the solvolysis of benzyl chloride

(The benzyl chloride concentration is 0·075 M throughout)

		$10^3 k_1$ (min.$^{-1}$)			
		50% aq. ethanol (48·35°)	60% aq. ethanol (48·35°)	70% aq. ethanol (55·15°)	80% aq. ethanol (82·25°)
$[HgCl_2]$	[NaCl]				
..	..	0·688	0·408	0·905	2·93
0·100	..	1·51	..	..	..
0·150	..	2·06	..	..	7·35
0·200	..	2·60	..	..	9·32
0·250	..	3·15	..	..	11·3
0·300	..	3·68	2·22	2·56	13·3
0·350	..	..	..	..	15·4
0·300	0·050	3·41	..	..	..
0·300	0·100	3·26	..	..	12·05
0·300	0·150	3·12	..	..	11·4
0·300	0·200	..	..	..	10·9

The Arrhenius parameters for the reactions are as follows (catalyst concentration for the catalysed reactions is throughout 0·3 M):

	Catalysed reaction E_A ; $\log_e B$	Normal reaction E_A ; $\log_e B$
50% aqueous ethanol	19·4; 24·76	20·4; 24·65
60% „ „	19·4; 24·25	20·7; 24·59
70% „ „	19·5; 23·92	20·8; 24·24

It has been shown that mercuric chloride selectively promotes nucleophilic aliphatic substitution by the S_N1 mechanism.[1] It has also been established that, benzyl chloride, which is on the S_N2–S_N1 border line, undergoes substitution in absence of catalyst chiefly by the S_N2 mechanism in the range of solvents under consideration.[4–5] That this is so is also evident from the fact that addition of hydroxide ions causes a marked increase in the rate; thus, addition of 0·08 M hydroxide ions causes the rate of the normal solvolysis in 50% aqueous ethanol to increase about five-fold. Since, a concentration of 0·3 M catalyst produces a five-fold increase in the rate of solvolysis in all the solvents, it can be concluded, that under these conditions, the S_N1 mechanism is dominant for the catalysed reaction. Thus, the normal and catalysed reactions can be formulated as follows:—

$$\left.\begin{array}{lcll} RCl + HgCl_2 & \overset{\text{slow}}{\rightleftharpoons} & R^+ + HgCl_3^- & \\ R^+ + HOX & \overset{\text{fast}}{\rightarrow} & ROX + H^+ & \end{array}\right\} S_N1 \text{ (catalysed)}$$

$$RCl + HOX \rightarrow ROX + HCl \qquad S_N2 \text{ (normal)}$$

That the principal catalytic agent at work is the unionised mercuric chloride molecule is clear from two points. Firstly, it is seen that the rate of reaction in presence of catalyst varies linearly with the catalyst concentration. Now, this is clearly unlikely if the catalysis is due to other derived species such as $HgCl^+$, Hg^{++}, etc., in view of the covalent nature of mercuric chloride and the fairly large concentrations employed. Secondly, although added chloride ions reduce the rate of the catalysed reaction somewhat, the magnitude of reduction is scarcely sufficient, if ionised forms of mercuric chloride are the catalysts, since the concentrations of chloride ions used here would certainly suppress all ionisation.

A study of the values of the Arrhenius parameters shows that the difference in the rates of the normal and catalysed reactions is chiefly due to the difference in the E_A values. Also, the variation in the rate of the catalysed reaction with solvent composition is almost wholly accounted for by changes in the frequency factor. Although caution is necessary in comparing the Arrhenius parameters for the two reactions since they proceed by different mechanisms, it seems reasonable to conclude that the catalyst functions through lowering the energy required for heterolysing the C–Cl bond. Support is lent to this conclusion by the fact that the E_A values for the catalysed reaction are significantly lower than the " normal " values for S_N1 reactions.

However, the most interesting point is the variation in the ratio of the rates of the normal and catalysed reactions with solvent and with temperature (Table II). In the calculation, since the total rate in presence of catalyst is partly due to the normal reaction, this rate has been subtracted from the total rate to give the rate due to the catalyst alone.

TABLE II

Variation in the ratio of the rates of normal and catalysed reactions

(The benzyl chloride and catalyst concentrations are 0·075 M and 0·300 M respectively)

$t°$ C.	Ratio of normal to catalysed rate			
	50% aq. ethanol	60% aq. ethanol	70% aq. ethanol	80% aq. ethanol
40·25	0·222	0·213	0·207	..
48·35	0·230	0·225	0·218	..
55·15	0·236	0·237	0·232	..
61·80	0·250	0·248	0·243	..
71·50	0·260	0·259	0·259	..
82·25	0·277	0·278	0·287	0·220

It is seen that (1) in every solvent, the value of the ratio rises steadily as the temperature increases, (2) at the lower temperatures, the ratio decreases as the solvent becomes less aqueous and (3) the rise in the value of the ratio with temperature is larger, the drier the solvent, so that as the temperature

is increased, there is a tendency for the rate to increase with decrease in the water content of the solvent.

According to the Hughes-Ingold theory, change to a better solvating medium should cause a large increase in the rates of both S_N1 and S_N2 reactions of the charge-type under consideration; and should favour the S_N1 at the expense of the S_N2 mechanism. Though some work has been done by Winstein[6] on the experimental determination of the variation of the rates of S_N1 reactions with solvent composition, not enough is known to treat the data on a quantitative basis. However, for our present purpose it is enough to note, in the range of solvents under consideration, that the magnitude of increase in rate for a fixed increase in the water content of the solvent decreases slightly as the solvent becomes more aqueous. Little is known regarding the behaviour of an S_N2 mechanism, but our results show that, benzyl chloride, at any rate, shows behaviour similar to the S_N1 mechanism; further, the behaviour is the same quantitatively for the normal reaction and the catalysed reaction, as shown in Table III.

Table III

(Temperature 82·25° C.; catalyst concentration for the catalysed reaction—0·300 M)

	50% aq. EtOH	60% aq. EtOH	70% aq. EtOH	80% aq. EtOH
Rate ($10^3 k_1$) (normal reaction)	14·55	8·95	5·45	2·90
Ratio of rates	1·63	1·64	1·88	
Rate ($10^3 k_1$) (catalysed reaction)	52·0	31·3	19·6	10·4
Ratio of rates	1·67	1·59	1·89	

In view of the above, and because the catalyst acts by causing a switch from the S_N2 to the S_N1 mechanism, it is reasonable to expect that the ratio of the normal reaction rate to that due to the catalyst should decrease as the solvent is made more aqueous. It has been seen, however, that the reverse is the case. Several factors may contribute to this result. Firstly, it has been assumed that the whole of the normal reaction proceeds by the S_N2 mechanism. Even in 50% aqueous acetone, which is a less polar solvent than 50% aqueous ethanol, Olivier[4] has shown that a part of the hydrolysis of benzyl chloride in presence of hydroxide ions proceeds by the S_N1 mechanism. It is therefore reasonable to conclude that at least in the more aqueous solvents under

consideration, the normal reaction has a duplex mechanistic character, the proportion of S_N1 falling as the water content of the solvent decreases. If allowance can be made in our calculation for this, it is obvious that there will be a tendency for the ratio considered above to reverse its order. Secondly, the introduction into the transition state of the bulky catalyst molecule is likely to result in some dispersion of charges, so that the rate may not show the sensitivity to solvent changes of a normal S_N1 reaction.

Incidentally, the gradual change of the ratio with solvent composition lends support to the view of Ingold[7] that the change from an S_N2 to an S_N1 mechanism is not sharp.

Experimental

Materials.—Mercuric chloride, sodium chloride and potassium iodide were reagent grade. Kauffmann C.P. benzyl chloride was carefully fractionated and used. x% aqueous ethanol signifies solvent made up of x volumes of dry ethanol and (100-x) volumes of water. Large stocks of solvents were made up to facilitate comparative measurements.

Kinetic method.—The appropriate quantity of benzyl chloride was taken in a 100 ml. graduated flask and made up with the solvent at room temperature. Where mercuric chloride or other salts were added, accurately weighed quantities were quantitatively transferred to the flask with the solvent. 5 ml. portions of the reaction mixture were sealed in ampoules and the ampoules immersed in the thermostat. One ampoule was vigorously shaken for 2 minutes and then taken out, chilled, washed, broken in a vessel and titrated

Table IV

Kinetics of the catalysed solvolysis of benzyl chloride in 80% aqueous ethanol, at 82·25° C.

[Benzyl chloride] = 0·0750 M; [$HgCl_2$] = 0·300 M

(Titres are expressed as ml. of 0·0375 N NaOH per 5·0 ml. samples of reaction mixture)

t (min.)	0	10	15	20	25	30	..	..
Titre	0·36	1·55	2·11	2·63	3·10	3·54	..	..
10^3k_1	..	13·2	13·4	13·4	13·4	13·4	..	..
t (min.)	35	40	45	50	55	60	65	70
Titre	3·94	4·39	4·72	5·06	5·40	5·66	5·91	6·22
10^3k_1	13·3	13·5	13·4	13·4	13·5	13·3	13·2	13·4
t (min.)	75	80	∞	..	..	..	..	..
Titre	6·42	6·68	10·00	..	..	..	..	..
10^3k_1	13·2	13·3	..	..	..	..	..	..

with alkali to a bromothymol blue end-point. When mercuric chloride was present, it was destroyed by the addition of a slight excess of a concentrated aqueous solution of potassium iodide (previously made neutral to the indicator), before titrating. The "infinity" titre was taken after a period equivalent to 8 half-lives. The rate values reported are the mean of two runs. The thermostat was of conventional design and the temperature could be controlled to $\pm 0{\cdot}05°$ C. or better. A typical run is illustrated in Table IV.

SUMMARY

The kinetics of the solvolysis of benzyl chloride, under catalysis by mercuric chloride, has been examined in a few compositions of aqueous ethanol. Some measurements in the absence of catalyst have also been carried out. The Arrhenius parameters have been determined for both the normal and catalysed reactions as also the effect of added chloride ions on the rates of the reactions. The results have been discussed in terms of the Hughes-Ingold theory of nucleophilic aliphatic substitution.

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REFERENCES

1. Bunton, C. A., Hughes, E. D. and Anantaraman, R. — Unpublished work; *see*, however, Ref. 7, pp. 359–60.
2. Anantaraman, R. .. *Bull. Cent. Res. Inst., Univ. Trav.*, 1955, **4 A** (1), 43.
3. (Miss) Saramma, K. and Anantaraman, R. — *Ibid.*, 1957, **5 A** (I), 30.
4. Olivier, S. C. J. *et al.* .. *Rec. trav. chim.*, 1934, **53**, 869, 891.
5. Kohnstam, G. *et al.* .. *J. Chem. Soc.*, 1957, 4747, 4970.
6. Winstein, S. *et al.* .. *J. Am. Chem. Soc.*, 1957, **79**, 1597, 1603, 4147.
7. Ingold, C. K. .. *Structure and Mechanism in Organic Chemistry* (Cornell University Press), 1953, p. 324.

EMISSION SPECTRUM OF CHLORINE EXCITED IN THE PRESENCE OF ARGON †

Part I. The Band System in the Region 2600–2390 Å

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Abstract

The spectrum of chlorine excited in the presence of argon has been photographed with a 21-ft. grating spectrograph in the first order. Two band systems in the region 2600–2390 Å and 2365–2239 Å are observed which appear to be respectively analogous to the 2950–2670 Å and 2660–2590 Å systems of bromine reported earlier by Venkateswarlu and Verma. The wavelengths and the wavenumbers of all the bands in the system 2600–2390 Å are given. The vibrational scheme along with the corresponding Franck-Condon parabola is also given. The analysis suggests that the lower state of the system is the $3\pi(O_u^+)$ state established by Elliott at 17658 cm.$^{-1}$ and that the upper state is at 57773 cm.$^{-1}$ The vibrational constants obtained are $\omega_0' = 246{\cdot}6$ cm.$^{-1}$, $\omega_0'x_0' = 0{\cdot}615$ cm.$^{-1}$, $\omega_0'' = 255{\cdot}2$ cm.$^{-1}$, $\omega_0''x_0'' = 5{\cdot}5$ cm.$^{-1}$, $\omega_0''y_0'' = -\,0{\cdot}0155$ cm.$^{-1}$ and $\omega_0''z_0'' = 0{\cdot}00115$ cm.$^{-1}$

Introduction

The emission spectrum of chlorine excited by means of a transformer discharge or high frequency electrodeless discharge is known to show a set of discrete bands in the region 6000–3900 Å and groups of continua in the region 3100–1850 Å. After a study of the rotational structure of some of the discrete bands in the visible region, Elliott and Cameron[1-2] attributed the discrete bands to the Cl_2^+ molecule. They were, however, able to put only half of the bands observed into a vibrational scheme. Harnath and Rao[3] are of the opinion that these discrete bands belong to four sub-systems. The discrete bands are being worked out in this laboratory with the higher orders of a 21-ft. grating spectrograph and the results obtained will be reported separately. The groups of continua were explained by Venkateswarlu[4] as arising due to transitions from upper stable states to different unstable states dissociating into $^2P + {}^2P$ normal chlorine atoms.

† Forms a part of the Ph. D. thesis of Baij Nath Khanna.
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Cameron and Elliott[5] excited chlorine in the presence of active nitrogen and reported 24 narrow diffuse bands superposing the original chlorine continuum in the region 2580–2400 Å.

Iodine and bromine when excited without the presence of a foreign gas are known to show groups of broad diffuse bands[6–9] which are due to transitions from upper stable states to lower unstable states dissociating into $^2P + {}^2P$ neutral atoms. It is also known that when these gases are excited in the presence of argon, the groups of diffuse bands fade away and new discrete band systems show up. Four such band systems were obtained earlier in iodine[10–11] and three recently in bromine.[12–14] Because of these interesting results in iodine and bromine, one is naturally tempted to expect similar results in chlorine. The spectrum obtained by exciting chlorine in the presence of argon is, therefore, studied and the results obtained are discussed in this paper.

EXPERIMENTAL DETAILS

Chlorine vapour was excited in the presence of argon by an uncondensed transformer discharge. The discharge tube, having nickel electrodes, was 40 cm. in length and 0·8 cm. in diameter and was made of pyrex glass. One end of it was fitted with a quartz window and was connected to a vacuum pump through a stop-cock. The other end was connected separately through stop-cocks to the sources of chlorine and argon. The discharge tube was fed with the chlorine gas prepared by heating anhydrous cupric chloride with an electric furnace to the temperature of nearly 300° C. Argon marked spectrally pure was obtained from Oxygen Acetylene Company.

It was found that as the pressure of argon in the discharge tube is increased, the original discrete bands of chlorine at 6000–3900 Å and the group of diffuse bands at 3100–1850 Å go down in intensity and a new spectrum appears. By adjusting the relative pressures of argon and chlorine inside the discharge tube, it was possible to eliminate the original spectrum (except for faint traces at the intense portions) and obtain only the new spectrum. When long exposures were needed, it was found necessary to cool the discharge tube with a table fan and flush the tube with fresh samples of chlorine and argon after every 6 hours, so as to avoid the continuum that overlaps the new systems.

Two band systems are obtained. One is a strong and extensive system in the region 2600–2390 Å and the other is a weak system in the region 2365–2239 Å. It was found that these systems could be well developed by adjusting the pressures of the constituent gases such that the discharge was bluish-

white in colour. It may be mentioned that the relative pressures were not measured in these experiments, but it was estimated that the pressure of argon was many times higher than that of chlorine.

The spectrum was photographed first on a Hilger Medium Quartz Spectrograph and then on a 21-ft. grating spectrograph in the first order. Fig. 1 shows the enlargement of the spectrum obtained with the 21-ft. grating spectrograph. The band system 2600–2390 Å only will be discussed in this paper. The bands of this system in general appear to be degraded towards longer wavelengths. There are also a number of bands for which the degradation is not clear. The wave-lengths and wavenumbers of the band heads are given in Table I along with their estimated relative intensities. As the band heads are not very sharp, the error in the measurements of their positions may be about $\pm$ 4 cm.$^{-1}$ The wavelengths of the 24 narrow diffuse bands obtained with a low dispersion instrument by Cameron and Elliott[5] in this region by exciting chlorine in the presence of active nitrogen are also included in the table for comparison. It appears likely that in the experiments of Cameron and Elliott, the new extensive band system was just beginning to show up and the continua were beginning to go down in intensity. The occurrence of this system in the excitation by active nitrogen suggests, as pointed out by Cameron and Elliott, that the emitter of the system is very likely Cl_2 and not Cl_2^+. This system appears to be analogous to the 3450–3040 Å system of iodine[11] and 2950–2670 Å system of bromine.[12]

TABLE I

Wavelengths, Wavenumbers and Relative Intensities of the Bands in the System 2600–2390 *Å*

Cameron and Elliott's		Present Experiments		Cameron and Elliott's		Present Experiments	
λ_{air}	I	λ_{air}	ν_{vac}	λ_{air}	I	λ_{air}	ν_{vac}
	1	2615·5	38222		2	2605·0	38976
	1	2614·9	38231		2	2603·2	38402
	1	2614·3	38240		1	2601·7	38425
	1	2613·5	38251		0	2601·2	38432
	0	2608·7	38321		0	2600·4	38440
	1	2607·4	38341		2	2599·9	38452
	1	2606·7	38351		2	2598·7	38469
	1	2605·7	38366		0	2596·8	38497

TABLE I—(*Contd.*)

Cameron and Elliott's		Present Experiments		Cameron and Elliott's		Present Experiments	
λ_{air}	I	λ_{air}	ν_{vac}	λ_{air}	I	λ_{air}	ν_{vac}
	2	2598·0	38480	2559·9	6	2560·5	39043
	2	2595·3	38520		4	2558·7	39071
	1	2595·1	38523		4	2558·1	39080
	1	2592·5	38561		8	2557·3	39092
	1	2591·0	38584		2	2555·6	39118
	1	2590·1	38597	2553·9	2	2554·0	39143
	4	2589·4	38607		3	2552·9	39159
	1	2588·5	38621		3	2551·7	39177
	1	2586·2	38655		6	2550·5	39196
	2	2585·1	38672		1	2549·8	39207
	4	2584·5	38681		1	2549·3	39215
	1	2583·7	38693		4	2548·5	39227
	0	2583·3	38699		2	2547·7	39239
	2	2582·2	38715		1	2546·8	39253
	4	2581·9	38720		4	2545·6	39272
2581·4	5	2581·2	38730	2545·0	6	2544·9	39283
	5	2580·8	38736		7	2543·5	39304
	1	2579·9	38750		2	2542·7	39317
	5	2578·4	38772		2	2541·5	39335
2577·3	0	2577·6	38784		1	2540·0	39358
	2	2577·0	38793		2	2538·8	39377
	5	2575·5	38816	2537·2	3	2537·6	39396
	4	2574·8	38826		1	2537·0	39405
	2	2573·7	38843		3	2536·0	39420
	4	2572·7	38858		1	2535·2	39433
	3	2572·2	38866		4	2534·4	39445
	3	2571·4	38878		1	2533·9	39453
	1	2569·3	38909		2	2532·4	39476
	10	2568·6	38920		2	2531·7	39487
2567·9	3	2568·3	38924		1	2530·2	39511
	2	2566·9	38946	2529·2	1	2529·6	39520
	3	2566·0	38960		3	2528·9	39531
	7	2565·1	38973		4	2528·1	39544
	4	2563·5	38998		2	2527·5	39553
	3	2561·4	39029		4	2526·4	39570

TABLE I—(*Contd.*)

Cameron and Elliott's		Present Experiments		Cameron and Elliott's		Present Experiments	
λ_{air}	I	λ_{air}	ν_{vac}	λ_{air}	I	λ_{air}	ν_{vac}
	1	2525·1	39591		3	2498·0	40020
	1	2524·6	39598		0	2496·8	40039
	2	2523·7	39612		3	2496·0	40052
	3	2522·7	39628		2	2495·4	40062
	2	2522·1	39638		2	2495·2	40065
2521·6	2	2521·6	39645		2	2494·5	40076
	1	2520·9	39656		2	2492·7	40105
	2	2520·0	39671	2491·7	1	2491·8	40119
	4	2519·0	39686		1	2491·3	40128
	4	2518·3	39697		2	2490·9	40134
	2	2517·2	39715		2	2490·3	40144
	1	2516·5	39726		4	2489·6	40155
	4	2515·3	39745		2	2489·1	40163
	5	2514·5	39757		2	2487·0	40197
	2	2513·6	39772		2	2486·6	40203
2513·5	3	2513·2	39778	2485·4	1	2485·6	40220
	3	2512·2	39794		1	2484·0	40246
	4	2511·4	39806		0	2483·3	40257
	2	2510·6	39819		1	2481·3	40289
	1	2509·7	39833		1	2480·7	40299
	1	2509·3	39840		3	2480·1	40309
	2	2508·8	39848		1	2478·5	40335
	2	2503·1	39859	2477·2	3	2477·2	40356
	1	2507·7	39865		2	2476·9	40361
	1	2507·3	39872		1	2476·4	40369
	1	2506·7	39881		4	2475·7	40380
2506·4	3	2506·0	39892		4	2474·6	40398
	3	2505·2	39905		1	2472·4	40434
	4	2504·7	39913		3	2472·0	40441
	2	2504·2	39921		1	2471·3	40452
	4	2503·3	39936	2470·0	1	2470·1	40472
	1	2501·7	39961		2	2469·5	40482
	1	2500·7	39977		2	2469·1	40488
2499·2	3	2499·9	39990		3	2468·7	40495
	2	2499·0	40004		2	2466·9	40525

TABLE I—(*Contd.*)

Cameron and Elliott's		Present Experiments		Cameron and Elliott's		Present Experiments	
λ_{air}	I	λ_{air}	ν_{vac}	λ_{air}	I	λ_{air}	ν_{vac}
	2	2466·3	40535		1	2439·1	40986
	1	2465·9	40541		3	2437·5	41013
	4	2464·5	40564	2434·3	3	2433·9	41074
	3	2463·0	40589		1	2433·7	41077
2462·2	3	2462·3	40600		2	2432·6	41096
	3	2461·9	40607		2	2431·6	41113
	2	2460·9	40623	2427·9	2	2426·8	41194
	2	2459·9	40640	2420·7	1	2420·1	41308
	1	2458·1	40670		2	2418·8	41330
	2	2457·6	40678		1	2417·4	41354
	1	2457·0	40688		1	2415·7	41383
	1	2455·3	40716		1	2413·5	41421
	2	2454·9	40723		1	2410·3	41476
	1	2454·5	40729	2405·9	2	2405·2	41564
	2	2452·2	40767		1	2404·5	41576
	0	2448·5	40829		2	2403·9	41586
2448·1	2	2448·0	40837		1	2402·4	41612
	2	2447·6	40844		2	2400·3	41649
	1	2446·8	40857	2392·8	1	2391·3	41805
	2	2445·2	40884		1	2390·9	41813
	2	2443·6	40911		1	2390·4	41821
	2	2440·8	40957				

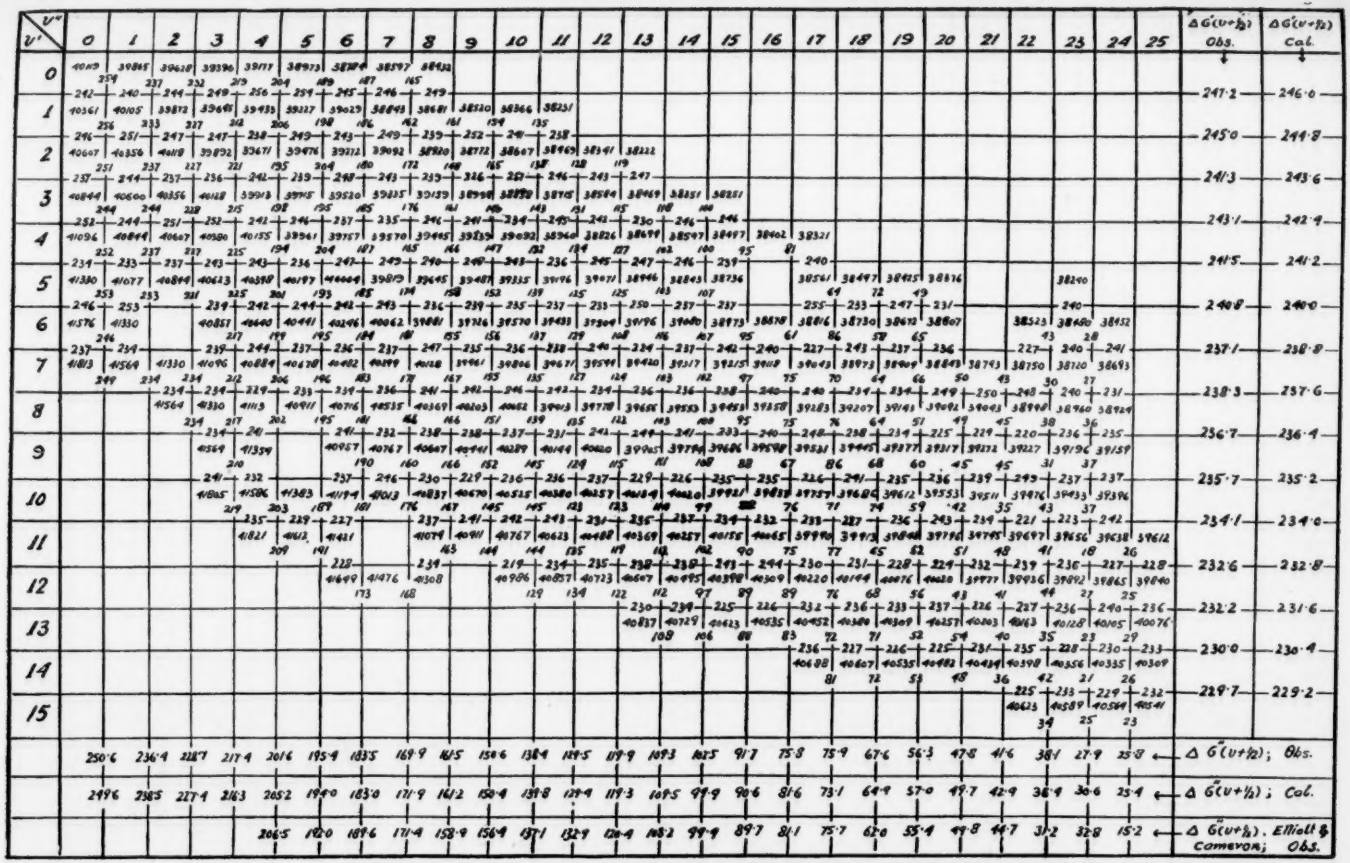
VIBRATIONAL ANALYSIS OF THE BAND SYSTEM 2600–2390 Å

The Deslandres scheme for the band system in the region 2600–2390 Å is given in Table II and the corresponding Franck-Condon parabola in Table III. As can be seen from Table II, the $\triangle G(v + \frac{1}{2})$ values obtained for the lower state of this system are in good agreement with those obtained by Elliott[15] for the upper state of the visible absorption bands of chlorine. All the bands could be fairly well represented by the formula

$$\nu = 40115 + (245{\cdot}6\, v' - 0{\cdot}615\, v'^2) - (255{\cdot}2\, v'' - 5{\cdot}5\, v''^2 - 0{\cdot}0155\, v''^3 + 0{\cdot}00115\, v''^4)$$

TABLE II. *Vibrational scheme of the 2600–2390 A system of Cl_2*

TABLE II. *Vibrational scheme of the 2600–2390 Å system of Cl_2*



The $\triangle G(v + \frac{1}{2})$ values calculated from the vibrational constants of this formula are included in Table II to facilitate comparison with the corresponding observed values. The lower state of the system is very likely the 3π (O_u^+) state[16] at 17658 cm.$^{-1}$ established by Elliott[15] from which the position of the upper state comes out to be 57783 cm.$^{-1}$

TABLE III

Intensity distribution and Franck-Condon parabola for the 2600–2390 Å system of Cl_2

v' \ v''	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
0	1	1	3	3	3	7	0	1	0																	
1	2	2	1	2	1	4	3	2	4	2	1	1														
2	3	3	1	3	2	2	4	8	10	5	4	2	1	1												
3	2	3	3	1	4	2	1	2	3	4	4	2	1	2	1	1										
4	2	2	3	4	4	1	4	4	1	2	8	3	4	0	1	0	2	0								
5	2	1	2	2	4	2	2	2	2	2	2	6	4	2	2	5		1	0	1	2			1		
6	1	2		1	2	3	1	2	1	1	4	1	7	6	4	7	3	5	5	2	4		1	2	2	
7	1	2	2	2	2	2	2	1	1	1	4	2	4	3	2	1	2	6	7	1	2	2	1	4	1	
8			2	2	2	2	1	2	1	2	3	4	3	1	2	1	1	6	1	2	8	6	4	3	3	
9				2	1		2	2	3	3	1	2	3	3	3	4	1	3	4	2	2	4	4	6	3	
10				1	2	1	2	3	2	1	2	4	0	2	3	2	1	4	4	2	1	1	2	1	3	
11					1	1	1		3	2	2	2	2	1	0	4	2	3	4	2	3	4	4	1	2	2
12							2	1	1		1	1	2	3	3	4	3	1	2	2	3	1	4	3	1	1
13														2	1	2	2	1	4	3	0	2	2	1	2	2
14																		1	3	2	2	1	4	3	1	3
15																							2	3	4	1

ISOTOPIC SHIFTS

There are three isotopic species $Cl^{35}Cl^{35}$, $Cl^{35}Cl^{37}$ and $Cl^{37}Cl^{37}$ for the chlorine molecule with the natural abundance ratio of 9·9 : 6·3 : 1. The bands corresponding to $Cl^{37}Cl^{37}$ are supposed to be much too weak to be observed with any certainty. It is expected that the bands corresponding to $Cl^{35}Cl^{35}$ will be accompanied by bands corresponding to $Cl^{35}Cl^{37}$ with a corresponding intensity ratio of 1·57 : 1. If one assumes that the vibrational analysis shown in Table II corresponds to $Cl^{35}Cl^{35}$ molecule, about 46 bands can be accounted to have isotopic components corresponding to $Cl^{35}Cl^{37}$. Table IV shows the observed and calculated values for the probable isotopic displacements. All the isotopic components can also be fitted well in the

TABLE IV

The Probable Isotopic Shifts for the Band System 2600–2390 Å

v', v''	ν in cm.$^{-1}$	I	Δ_ν (obs.) cm.$^{-1}$	Δ_ν (cal.) cm.$^{-1}$
6, 24	38440	0	12	12
	38452	2		
2, 11	38469	2	11	13
	38480	2		
6, 23	38469	2	11	10
	38480	2		
3, 12	38584	1	13	11
	38597	1		
2, 10	38607	4	14	12
	38621	1		
7, 25	38655	1	17	16
	38672	2		
1, 8	38681	4	18	14
	38699	0		
2, 9	38772	5	12	12
	38784	0		
7, 21	38784	0	9	11
	38793	2		
3, 10	38858	4	8	9
	38866	3		
8, 23	38946	2	14	17
	38960	3		
8, 21	39029	3	14	14
	39043	6		
8, 20	39080	4	12	13
	39092	8		
9, 23	39177	3	19	20
	39196	6		
9, 22	39207	1	20	18
	39227	4		
1, 5	39227	4	12	10
	39239	2		
9, 21	39253	1	19	17
	39272	4		
0, 3	39396	3	9	9
	39405	1		
9, 18	39433	1	12	13
	39445	4		
9, 16	39591	1	7	11
	39598	1		
10, 19	39598	1	14	17
	39612	2		
0, 2	39628	3	10	6
	39638	2		

TABLE IV—(*Contd.*)

v', v''	ν in cm.$^{-1}$	I	Δ_ν (obs.) cm.$^{-1}$	Δ_ν (cal.) cm.$^{-1}$
11, 24	39612	2	26	27
	39638	2		
10, 18	39671	2	15	16
	39686	4		
11, 22	39671	2	26	24
	39697	4		
11, 21	39726	1	19	23
	39745	4		
11, 20	39772	2	22	22
	39794	3		
11, 19	39833	1	15	20
	39848	2		
12, 24	39833	1	32	30
	39865	1		
12, 23	39859	2	33	29
	39892	3		
9, 13	39892	3	13	9
	39905	3		
11, 18	39892	3	21	19
	39913	4		
8, 11	39905	3	8	6
	39913	4		
11, 17	39977	1	13	18
	39990	3		
10, 14	40004	2	16	12
	40020	3		
13, 25	40039	0	37	35
	40076	2		
11, 15	40144	2	11	16
	40155	4		
13, 18	40356	3	24	25
	40380	4		
12, 15	40380	4	18	19
	40398	4		
12, 24	40472	1	23	18
	40495	3		
12, 13	40589	3	18	18
	40607	3		
3, 0	40829	0	15	11
	40844	2		
4, 0	41077	1	19	14
	41096	2		
8, 4	41096	2	17	16
	41113	2		
5, 0	41308	1	22	18
	41330	2		
8, 3	41308	1	22	17
	41330	2		

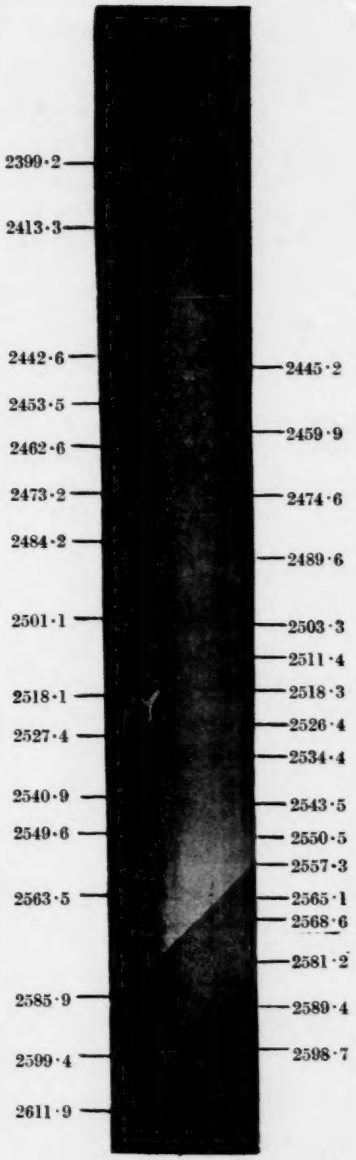


Fig. 1. Enlargement of the 2600–2390 Å system of Cl_2 excited in the presence of argon taken with a 21-ft. grating spectrograph in the first order.

vibrational scheme of Cl^{35} Cl^{35} with different (v', v'') values and are also shown as such in Table II. It is probably because of such overlapping that the relative expected intensity variation of 1·57: 1 is not maintained in Table IV and therefore the identification of the isotopic displacements can not be said to be completely unambiguous.

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References

1. Elliott, A. and Cameron, W. H. B. .. *Proc. Roy. Soc.* (*Lond.*), 1937, **158 A**, 681.
2. ———— .. *Ibid.*, 1938, **164**, 531.
3. Haranath, P. B. V. and Rao, P. T. .. *Curr. Sci.*, 1956, **25**, 47.
4. Venkateswarlu, P. .. *Proc. Ind. Acad. Sci.*, 1947, **26 A**, 22.
5. Cameron, W. H. B. and Elliott, A. .. *Proc. Roy. Soc.* (*Lond.*), 1938–39, **169 A**, 463.
6. Venkateswarlu, P. .. *Proc. Ind. Acad. Sci.*, 1946, **24 A**, 480.
7. ———— .. *Ibid*, 1947, **25 A**, 119.
8. ———— .. *Ibid.*, 1947, **25 A**, 133.
9. ———— .. *Ibid.*, 1947, **25 A**, 138.
10. Waser, J. and Wieland, K. .. *Nature*, 1947, **160**, 643.
11. Venkateswarlu, P. .. *Phys. Rev.*, 1951, **81**, 821.
12. Venkateswarlu, P. and Verma, R. D. .. *Proc. Ind. Acad. Sci.*, 1957, **46 A**, 251.
13. ———— .. *Ibid.*, 1957, **46 A**, 416.
14. Verma, R. D. .. *Ibid.*, 1958, **47 A**, 196.
15. Elliott, A. .. *Proc. Roy. Soc.* (*Lond.*), 1930, **127 A**, 638.
16. Mulliken, R. S. .. *Phys. Rev.*, 1934, **46**, 549.

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